sociation constant values of $K^{\mathrm{DPAH}}{}_{\mathrm{A}} = 5.42 \times 10^{-5}$[5] and $K^{\mathrm{pyH^+}}{}_{\mathrm{A}} = 5.37 \times 10^{-6}$ dm^3·mol^{-1},[10] the two unknowns are k_1 and k_2.

Activity coefficients, f, calculated from the Debye–Hückel limiting law were used in the equilibrium calculations for the ionic species. Changes in ionic strength due to relaxation were negligibly small[11] so $k_{-3} = k_{-3}°f^2$ and k_2 was calculated as $k_2 = k_2°f^2$, but higher order activity corrections were neglected. The experimental activities and relaxation times are summarized in Table I.

It has been shown recently that small amounts (0.1–0.3%) of water can significantly alter conductivities and stability constants of acids in alcohol solutions.[12] However, no systematic deviations of decay times from those reported in Table I are detectable when a sample solution is deliberately made 0.1% and then 1.0% by weight water. This chemical system should be comparatively insensitive to perturbations by water since the rate of protonation of the dipicrylamine anion is limited not by rotation of protonated solvent molecules but rather by steric interference of nitro groups on the anion.[8,13]

The equations for τ_{I}^{-1} and τ_{II}^{-1} were programmed on an LSI-11 computer. The values for k_1 and k_2 were iteratively incremented, calculating $\tau_{\mathrm{theory}} - \tau_{\mathrm{exptl}}$ for each solution. Final values of k_1 and k_2 were obtained at the minimum in the standard deviation. Solution no. 6 was discarded in the final calculations for reasons discussed below.

Two adverse conditions can arise in a chemical system of this kind. First, one may have observed τ_{I}^{-1} instead of τ_{II}^{-1} in all or some of the solutions. However, the standard deviation obtained when the data are fitted to eq 5 is in all cases much higher than that obtained for eq 6 for individual solutions and combinations of solutions. Furthermore, the rate constants obtained are physically meaningless, k_1 being several orders of magnitude above the theoretically highest possible value for a diffusion-controlled reaction. Second, one may have observed a mixture of τ_{I} and τ_{II}, if τ_{I} is close to τ_{II} in value. Two independent facts rule out this possibility as well: the decay time in each case was calculated repeatedly from each set of data, shifting the data window by two points each time. No systematic deviation was observed in the calculated τ value.[14] In addition, reaction capacity factors (which are proportional to the amplitudes) and amplitude ratios of the two normal modes were calculated by using the formalism described by Purdie et al.[15] In all cases except no. 6, the ratio of amplitude II to amplitude I was greater than 8. The reaction capacity factor of the first normal mode was also largest for no. 6. Solution no. 6 was therefore not used in the final calculation of the rate constants. The values obtained for k_1 and k_2 were as follows: $k_1 = (1.57 \pm 0.32) \times 10^{10}$ dm^3·mol^{-1}·s^{-1} and $k_2 = (1.71 \pm 0.34) \times 10^8$ s^{-1}, giving $k_{-1} = k_1K^{\mathrm{pyH^+}}{}_{\mathrm{A}} = (8.43 \pm 1.69) \times 10^4$ dm^3·mol^{-1}·s^{-1} and $k_{-2} = k_2K^{\mathrm{DPAH}}{}_{\mathrm{A}}/K^{\mathrm{pyH^+}}{}_{\mathrm{A}} = (1.72 \pm 0.34) \times 10^9$ dm^3·mol^{-1}·s^{-1}. From the rate constant k_1 of the diffusion-controlled protonation of pyridine a reaction distance of 3.9 Å is calculated. This is larger than those of the methyl-substituted pyridines. If the requirement for proper orientation of the reactants[9] is taken into account, the agreement is in this case better with the mechanism of 5 than with that of eq 6. The deprotonation rate constant is 1 order of magnitude higher than those determined by Cocivera for methyl-substituted pyridines,[1] reflecting the lower basicity of unsubstituted pyridine in methanol.

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Supplementary Material Available: Details of the reaction capacity factor and amplitude ratio calculation (9 pages) are available. Ordering information is given on any current masthead page.

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Photoreduction of Hemin in Alcohol-Containing Mixed Solvents

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Abstract: The photochemical behavior of chlorohemin, iron(III) protoporphyrin IX chloride, in deaerated aqueous solutions containing 18% v/v pyridine and varying types and concentrations of alcohols has been investigated. When the alcoholic component of the solvent was methanol, ethanol, or 2-propanol, ultraviolet irradiation caused the reduction of the Fe(III) complex to bis(pyridine)(protoporphyrin IX)iron(II). When the alcohol was *tert*-butyl alcohol, no photoreduction was observed upon continuous irradiation. The study of the dependence of quantum yields on irradiation wavelength, pH, and alcohol concentration, as well as flash photolysis experiments, led to formulation of a photoreduction mechanism involving photochemical electron transfer from the alcohol to the Fe(III) center (with or without intervening ·OH radicals), followed by secondary reactions of the alcohol-derived radicals.

Introduction

Owing to their biological importance metalloporphyrin complexes have been widely studied.[1,2] In particular, considerable attention has been given to their redox activity because of the role played by these compounds in biological systems as electron carriers. As far as the photochemical behavior of metalloporphyrins is concerned, the greatest interest has been devoted to the magnesium porphyrins in connection with the photosyntetic processes,[3] however, in recent years some metalloporphyrin com-

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plexes other than the magnesium porphyrins have been the subject of photochemical studies.[4,5] Strikingly, only scattered attention[6-14] has been paid to the photochemical behavior of systems containing iron porphyrins in spite of their biological importance. Actually, most of the systems studied are complex, naturally occurring molecules, in which the photochemistry is likely to be affected by the presence of the proteic moieties. On the other hand, very few specific investigations on the photochemistry of isolated iron porphyrin chromophores have been reported to date.[15] Most probably, this is due to the inherent difficulties of these systems, which are generally affected by very complex chemical equilibria and aggregation phenomena.[16]

We have now undertaken a systematic investigation on the photochemical behavior of iron prophyrin complexes. We report here the results obtained in the study of the photoreduction of iron(III) protoporphyrin IX in hydroalcoholic solvents.

Experimental Section

Materials. Chlorohemin, iron(III) protoporphyrin IX chloride ($Fe^{III}PPCl$), was obtained from Fluka AG and was used without further purification. The other chemicals used were commercial products of reagent grade. The solvents used were commercial products of spectrograde quality.

Solutions of bis(pyridine)(protoporphyrin IX)iron(II) ($Fe^{II}PP(py)_2$) were prepared in situ by reducing deaerated aqueous solutions of Fe^{III}-PPCl containing 18% v/v (2.3 M) pyridine,[17] with excess $Na_2S_2O_4$.

Apparatus. The irradiation equipment used to obtain 313, 334, 365, and 404-nm light was as previously described.[18] The reaction cells were standard 1-cm spectrophotometric cells fitted with glass stopcocks and contained in thermostated cell holders. The temperature of the irradiated solutions was always maintained at 5 ± 0.5 °C by using Colora NB 35 124-TK 64 thermostatic-cryogenic equipment. Spectrophotometric measurements were performed with Perkin-Elmer Model 323 (double beam) and Shimadzu QV 50 (single beam) spectrophotometers. The detection of fast reactions was accomplished with an Applied Photophysics KR-10 flash-kinetic spectrophotometer. Gas chromatographic analyses were performed with a Perkin-Elmer Model F 17 gas chromatograph, using a Porapak T, 80–100 mesh, column.

Procedures. Two standard solvent systems were used: (a) 18% v/v (2.3 M) pyridine/water and (b) 18% v/v pyridine/40% v/v alcohol/42% v/v water (alcohol = methanol, ethanol, 2-propanol, or *tert*-butyl). The solution used in the photochemical runs was prepared by dissolving chlorohemin in the appropriate solvents. The pH of the solutions, as measured with a glass electrode, was adjusted to the desired value by addition of NaOH. These solutions were used within 24 h after the preparation; during this period no appreciable variations in the absorption spectrum were observed. Solutions aged for long-time periods underwent aggregation phenomena[19] which quantitatively affected the photochemical results. The solutions were deaerated before irradiation by bubbling pure nitrogen for 45 min. During the irradiation the solutions were stirred by a stream of nitrogen from a glass capillary. The photoreaction quantum yields were calculated from kinetic runs under zero-order experimental conditions. The light intensity was measured by the ferrioxalate actinometric method[20] in the reaction cell before and after each photochemical run.

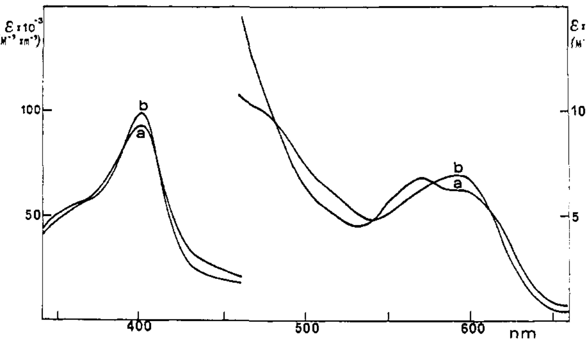

Figure 1. Absorption spectra of $Fe^{III}PPCl$ dissolved in (a) 18% v/v pyridine/water and (b) 18% v/v pyridine/40% v/v ethanol/42% v/v water at pH 12.5.

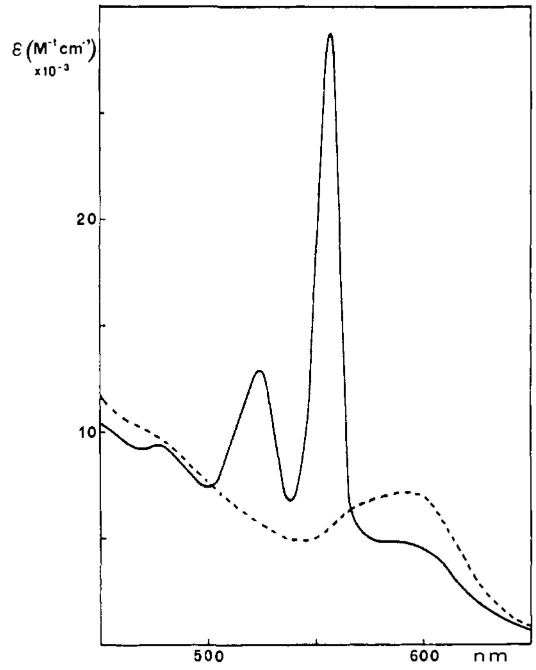

Figure 2. Absorption spectrum of $Fe^{II}PP(py)_2$ in 18% v/v pyridine/40% v/v ethanol/42% v/v water at pH 12.5. The spectrum of $Fe^{III}PPCl$ dissolved in the same solvent (dashed line) is reported for comparison.

Flash photolysis experiments, performed to detect fast-reaction steps, were performed in a Pyrex reaction cell (10-cm pathlength, 2-cm diameter) in order to avoid light absorption by pyridine. Transient spectral changes were measured by point by point wavelength variations. The solution was changed after every flash under nitrogen.

Results

The absorption spectra of chlorohemin ($Fe^{III}PPCl$) in solvents a and b (alcohol = ethanol, see Procedures) at pH 12.5 are reported in Figure 1. According to previous reports,[21] the absorption spectra of $Fe^{III}PPCl$ recorded by using methanol or 2-propanol as the alcoholic component of solvent system b are quite similar to that obtained by using ethanol (Figure 1, curve b), while *tert*-butyl alcohol does not substantially affect the alkaline spectrum with respect to alcohol-free a solvent (Figure 1, curve a).

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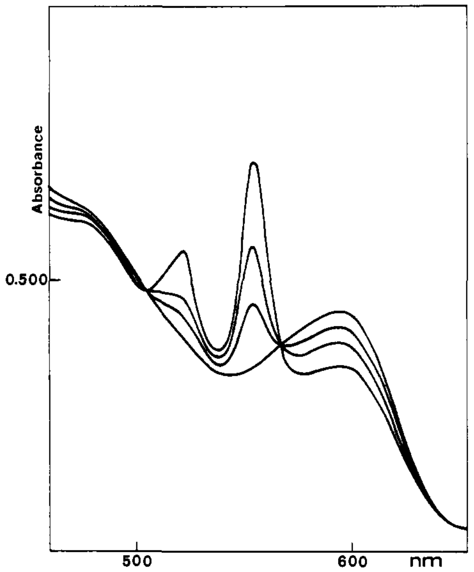

Figure 3. Visible spectral changes observed upon 365-nm irradiation of 6.0×10^{-5} M deaerated solutions of $Fe^{III}PPCl$ in 18% v/v pyridine/40% v/v ethanol/42% v/v water at pH 12.5.

Figure 2 shows the absorption spectrum of bis(pyridine)(protoporphyrine IX)iron(II) ($Fe^{II}PP(py)_2$) in solvent b. The spectrum is independent of pH in the range 8–13 and of the type and concentration of the alcoholic solvent.

Photochemical Behavior upon Continuous Irradiation. When a deaerated solution of $Fe^{III}PPCl$ in solvent b (alcohol = ethanol) at pH 12.5 was irradiated with 365-nm light, the green color of the solution changed gradually to blood(!)-red. The corresponding spectral variations are shown in Figure 3. A comparison of these spectra with those in Figure 2 (isosbestic points at 504 and 566 nm) clearly indicates that the photoreaction is a clean photoreduction of the Fe(III) species to $Fe^{II}PP(py)_2$. The same photochemical behavior was observed when methanol or 2-propanol was used instead of ethanol as the alcoholic component of solvent b. On the other hand, no appreciable spectral changes were observed to occur for comparable irradiation periods when *tert*-butyl alcohol was used instead of ethanol. No spectral changes were observed in the absence of alcohols (solvent a). Negligible spectral changes[22] could only be detected by irradiation of aerated solvent b solutions. Gas chromatographic analysis performed after irradiation of $Fe^{III}PPCl$ in solvent b (alcohol = ethanol) clearly revealed the presence of appreciable amounts of acetaldehyde as product. Similar experiments, performed with methanol or 2-propanol, did not allow us to identify the corresponding oxidation products (formaldehyde and acetone, respectively) because of either inadequate separation in the chromatographic column or presence of the products as impurities in the alcohol used.

Flash Photolysis. The results obtained by flash photolysis experiments on solutions of $Fe^{III}PPCl$ can be summarized as follows:

(i) Deaerated Solution: Solvent b (Alcohol = Ethanol, Methanol, or 2-propanol; pH 12.5). The behavior is qualitatively the same with the three alcohols. The flash gives rise to an instantaneous primary absorbance change (time scale < 30 μs) which is followed by a slower secondary one in the millisecond time scale. The results obtained with ethanol in solvent b are reported, as an example of such general behavior, in Figure 4. If both primary and secondary absorbance changes are reported as a function of wavelength, spectral variations of the type shown in Figure 5 (curves a and b) are obtained. The comparison with the different spectrum (curve c) obtained from the spectra in Figure 2 indicates that both the primary and secondary reactions observed in the flash photolysis of this solution correspond to the reduction of the initially present Fe(III) species to $Fe^{II}PP(py)_2$.

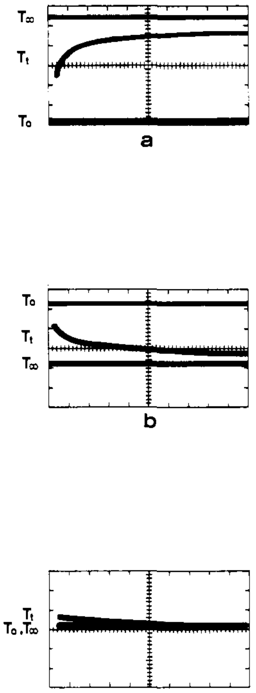

Figure 4. Flash photolysis of deaerated solutions of $Fe^{III}PPCl$ in 18% v/v pyridine/40% v/v alcohol/42% water at pH 12.5 (T_0, T_∞, and T_t are initial, final, and transient trasmittance signals, respectively). Transmittance decreases along the vertical axis. Vertical scale = 5% transmittance change/division; horizontal scale = 0.5 ms/division: (a) alcohol = ethanol, 554 nm, $T_0 = 0.50$; (b) alcohol = ethanol, 600 nm, $T_0 = 0.46$; (c) alcohol = *tert*-butyl alcohol, 554 nm, $T_0 = 0.22$.

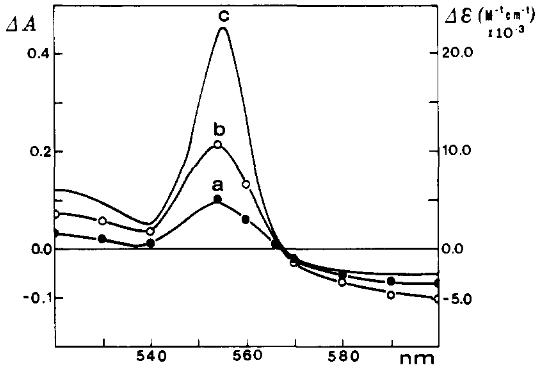

Figure 5. Differential spectral variations obtained from flash photolysis of $Fe^{III}PPCl$ dissolved in 18% v/v pyridine/40% v/v ethanol/42% v/v water at pH 12.5 (left scale): (a) 0.02 ms after the flash; (b) 5 ms after the flash. Curve c shows the difference spectrum of Fe(III) and Fe(II) complexes in the experimental conditions used (right scale).

(ii) Deaerated Solution: Solvent b (Alcohol = *tert*-Butyl Alcohol; pH 12.5). The flash gives rise to a primary fast absorbance change (time scale < 30 μs) which is qualitatively the same as that observed with the other alcohols (point i), although the absorbance changes are much smaller (10–20%) than in the previous case. In this case, however, the absorbance change is a transient one, since the first process is followed by a secondary one in the millisecond time scale which brings back the absorbance to the initial value.

(iii) Deaerated or Aerated Solution: Solvent a (pH 12.5). The flash does not give rise to any absorbance change.

(iv) Aerated Solution: Solvent b (Alcohol = Methanol, Ethanol, or 2-Propanol; pH 12.5). In the microsecond to millisecond time scale the behavior is the same as that described in point i. In this case, however, a slow reaction, taking place after the flash in the second time scale, reverts the absorbance of the solution to the initial value.

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(22) Aerated solutions undergo a slow bleaching process, which is related to photodecomposition of the porphyrin ring.[23]

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Table I. Photoreduction Quantum Yields of $Fe^{III}PPCl$ in Water/Alcohol Solutions Containing 18% v/v Pyridine

alcohol	λ_{irr}, nm	alcohol, % v/v	pH	$10^3\Phi$
methanol	365	40	12.5	1.8
2-propanol	365	40	12.5	5.0
tert-butyl alcohol	365	40	12.5	$<10^{-2}$
ethanol	365	40	12.5	5.0
ethanol	313	40	12.5	5.5
ethanol	404	40	12.5	1.8
ethanol	436	40	12.5	0.1
ethanol	365	20	12.5	1.7
ethanol	365	30	12.5	2.7
ethanol	365	50	12.5	6.0
ethanol	365	60	12.5	6.4
ethanol	365	40	8.9	~0.1
ethanol	365	40	9.8	1.2
ethanol	365	40	11.0	3.6
ethanol	365	40	11.8	4.8
ethanol	365	40	12.8	5.1
ethanol	365	40	13.1	5.1

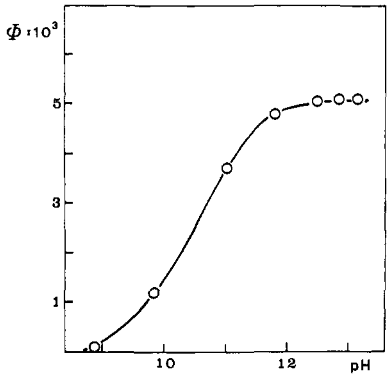


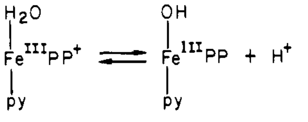
Figure 6. Dependence of the photoreduction quantum yield on pH. $Fe^{III}PPCl$ concentration = 6.0×10^{-5}M; solvent = 18% v/v pyridine/40% v/v ethanol/42% v/v water.

Quantum Yields. The quantum yields of the photochemical reduction were spectrophotometrically measured.[24] The results are shown in Table I as a function of the nature of the alcoholic component of the mixed solvent, irradiation wavelength, alcohol concentration, and pH. The quantum yield values of Table I were independent of the $Fe^{III}PPCl$ concentration in the 6.0×10^{-6}–1.0×10^{-4} M range and of the absorbed light intensity in the 6.8×10^{-10}–2.7×10^{-8} einstein s^{-1} cm^{-3} range.

The dependence of the quantum yield on pH is also graphically represented in Figure 6.

Discussion

Identification of the Photoreducible Species. In a previous study[21] it has been concluded that when $Fe^{III}PPCl$ is dissolved in a or b solvent, the dominant species is the aquopyridine axially substituted complex, which undergoes an acid–base equilibrium (eq 1) with $pK_a = 10.5$.


(1)

$$\underset{py}{\overset{H_2O}{Fe^{III}PP^+}} \rightleftharpoons \underset{py}{\overset{OH}{Fe^{III}PP}} + H^+ \qquad (1)$$

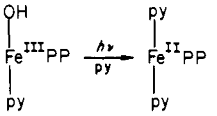
The photoreduction quantum yield values obtained as a function of pH (Figure 6) fall on a titration-like curve with an apparent p*K* of 10.7. This suggests that, although both species in Figure 1 absorb the excitation light, only the basic one is photoreducible. As a consequence the values reported in Table I and Figure 6 correspond to apparent quantum yields since they are calculated by using the intensity of excitation light absorbed by both components of the irradiated solution. The apparent quantum yield values coincide with the actual ones at pH ≥ 12 where the excitation light is completely absorbed by the photoreducible species.

Table II. Redox Potentials of Some Radicals in Aqueous Solution[a]

RHOH	·ROH	$E_1°$,[b] V	$E_2°$,[c] V
methanol	$\cdot CH_2OH$	1.29	−0.92
ethanol	$CH_3\dot{C}HOH$	0.95	−0.61
2-propanol	$CH_3\dot{C}(OH)CH_3$		−1.2
tert-butyl alcohol	$(CH_3)_2COH$–$\dot{C}H_2$	0.6	−0.1
water	·OH	2.8	

[a] From ref 27; solvent = water; vs. NHE. [b] $ROH + e^- + H^+ \rightarrow RHOH$. [c] $ROH^+ + e^- \rightarrow \cdot ROH$.

On the basis of the above considerations the photoreduction of $Fe^{III}PPCl$ in solvent b may be well described by the overall equation:


(2)

$$\underset{py}{\overset{OH}{Fe^{III}PP}} \xrightarrow[py]{h\nu} \underset{py}{\overset{py}{Fe^{II}PP}} \qquad (2)$$

Photoreduction Mechanism. In the following discussion, alcohols and alcohol-derived radicals will frequently appear. It is difficult to find a unique set of symbols holding for primary, secondary, and tertiary alcohols and radicals. The following policy has been used in writing eq 4 and all the following. The alcohol, the ketyl radical, and the alkoxy radical have been designated as R_1R_2CHOH, $R_1R_2\dot{C}OH$, and $R_1R_2CHO\cdot$, respectively. This notation holds for methanol ($R_1 = R_2 = H$), ethanol ($R_1 = H$, $R_2 = CH_3$), and 2-propanol ($R_1 = R_2 = CH_3$) and for the related radicals. When the alcohol is *tert*-butyl alcohol the equations should be used by replacing the ketyl radical with the hydroxy-*tert*-butyl radical $(CH_3)_2C(OH)\dot{C}H_2$ and by writing the alkoxy radical as $(CH_3)_3CO\cdot$.

There can be no doubt that the alcohols play a fundamental role in the photoreduction of $Fe^{III}PP(py)(OH)$. The inefficiency of photoreduction in the absence of alcohol and the detection of acetaldehyde as a photoreaction product in ethanol-containing solvent demonstrate this point.

Flash photolysis experiments show that (i) in addition to $Fe^{II}PP(py)_2$ a species is formed in the primary photochemical reduction which thermally reduces the $Fe^{III}PP(py)(OH)$ reactant to $Fe^{II}PP(py)_2$; since in the absence of alcohol no photoreduction is observed to occur, it is reasonable to suppose that a ketyl radical is the reducing intermediate which gives rise to the secondary reduction;[25] and (ii) *tert*-butyl alcohol has an anomalous behavior in comparison with the other alcohols in that the primary photoreduction is less efficient and is followed by rapid reoxidation of the reduction product $Fe^{II}PP(py)_2$; this indicates that *tert*-hydroxybutyl radicals prefer to reoxidate the product of the primary photoreduction rather than reduce the $Fe^{III}PP(py)(OH)$ reactant. The intrinsic ability of the above mentioned alcohol-derived radicals to behave as oxidizing or reducing agents is measured by the redox potentials ($E_1°$ and $E_2°$, respectively) reported in Table II. The redox potential for reaction 3 is reported

$$Fe^{III}PP(py)(OH) + py + e^- \rightarrow Fe^{II}PP(py)_2 + OH^- \qquad (3)$$

to be ~−0.15 V.[1] This suggests that the substantial difference in the behavior of *tert*-hydroxybutyl radical with respect to the other alcohol-derived (ketyl) radicals reported in Table II comes from the fact that ketyl radicals from methanol, ethanol, and 2-propanol, which have $E_1° > -0.15$ and $E_2° < -0.15$, are able to oxidize $Fe^{II}PP(py)_2$ as well as to reduce $Fe^{III}PP(py)(OH)$

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(24) Since the spectrum of the $Fe^{III}PPCl$ reactant depends on several experimental variables,[21] care was taken to use in the calculations the extinction coefficients appropriate to the experimental conditions used.

(25) A similar role of ketyl radicals was observed by Walling in his extensive studies on the oxidation of alcohols in Fe^{2+}–H_2O_2 systems.[26]

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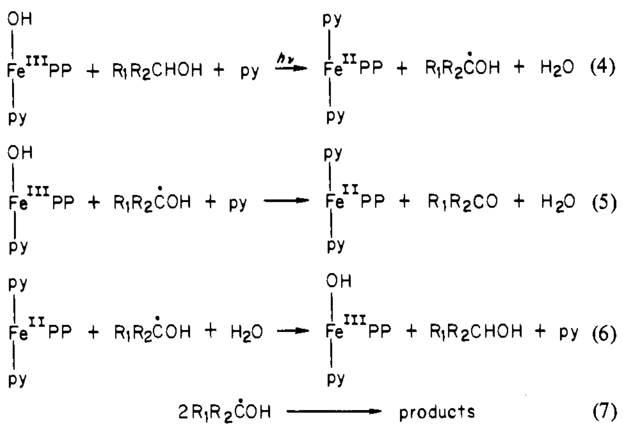
Scheme I



$$\overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} + \mathrm{R_1R_2CHOH} + \mathrm{py} \xrightarrow{h\nu} \overset{\mathrm{py}}{\underset{\mathrm{py}}{\mathrm{Fe^{II}PP}}} + \mathrm{R_1R_2\dot{C}OH} + \mathrm{H_2O} \tag{4}$$

$$\overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} + \mathrm{R_1R_2\dot{C}OH} + \mathrm{py} \longrightarrow \overset{\mathrm{py}}{\underset{\mathrm{py}}{\mathrm{Fe^{II}PP}}} + \mathrm{R_1R_2CO} + \mathrm{H_2O} \tag{5}$$

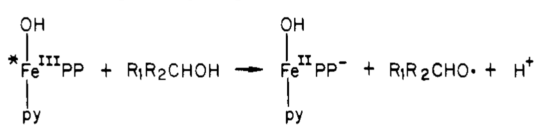
$$\overset{\mathrm{py}}{\underset{\mathrm{py}}{\mathrm{Fe^{II}PP}}} + \mathrm{R_1R_2\dot{C}OH} + \mathrm{H_2O} \longrightarrow \overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} + \mathrm{R_1R_2CHOH} + \mathrm{py} \tag{6}$$

$$2\mathrm{R_1R_2\dot{C}OH} \longrightarrow \text{products} \tag{7}$$

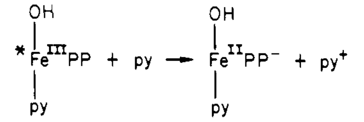
whereas *tert*-hydroxybutyl radicals ($E_1° > -0.15$, $E_2° \simeq -0.15$) are much more inclined to oxidize Fe$^{\mathrm{II}}$PP(py)$_2$ than to reduce Fe$^{\mathrm{III}}$PP(py)(OH). The above considerations can be schematized as Scheme I, where eq 4 is meant to represent all the fast (submicrosecond time scale) processes which we will formally designate as "the primary photochemical" process. For methanol, ethanol, and 2-propanol, reactions 5 and 6 can occur in competition and their net result is the secondary thermal reduction of Fe$^{\mathrm{III}}$PP(py)(OH) detected in the flash photolysis experiments; when the alcohol is *tert*-butyl alcohol, reaction 5 is thermodynamically unfavorable and the reoxidation of Fe$^{\mathrm{II}}$PP(py)$_2$ formed in the primary photoreduction is the only secondary thermal process observed in the flash experiments.

The flash results (Figure 4) show that the secondary thermal process has about the same efficiency as the primary photoreaction. This indicates that in the flash photolysis experimental conditions the second-order radical processes (eq 6 and 7) are quite inefficient with respect to the pseudounimolecular one (eq 5). In continuous irradiation, the experimental conditions used (lower excitation light intensity and higher Fe$^{\mathrm{III}}$PP(py)(OH) reactant concentration) are even more favorable to unimolecular processes. Thus, the following experimental results are easily explained. (a) The overall photoreduction quantum yield is independent of excitation light intensity and of reactant concentration. (b) No alcohol reaction products other than the aldehydes are experimentally detected after irradiation. According to this picture, the photoreduction quantum yields reported in Table I are practically twice the primary photoreduction quantum yield values.

It is now possible to discuss in detail the intimate mechanism of the "primary photochemical" act (eq 4). At least four mechanisms can be proposed for this process. (i) Bimolecular electron transfer from alcohol (eq 8) or pyridine (eq 9)[28] to the excited state of the Fe(III) complex. In these cases fast scavenging of the alkoxy (eq 10)[29] or pyridine radical cation (eq 11) by alcohol must follow the primary step.



$$^{*}\overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} + \mathrm{R_1R_2CHOH} \longrightarrow \overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{II}PP^{-}}}} + \mathrm{R_1R_2CHO\cdot} + \mathrm{H^+} \tag{8}$$

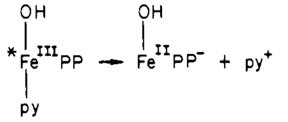


$$^{*}\overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} + \mathrm{py} \longrightarrow \overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{II}PP^{-}}}} + \mathrm{py^+} \tag{9}$$

$$\mathrm{R_1R_2CHO\cdot} + \mathrm{R_1R_2CHOH} \rightarrow \mathrm{R_1R_2CHOH} + \mathrm{R_1R_2\dot{C}OH} \tag{10}$$

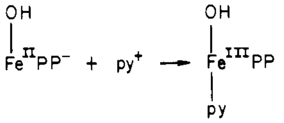
$$\mathrm{py^+} + \mathrm{R_1R_2CHOH} \rightarrow \mathrm{pyH^+} + \mathrm{R_1R_2\dot{C}OH} \tag{11}$$

Bimolecular redox reactions of excited states of transition-metal complexes are widely occurring phenomena,[31] and some reactions of this type, involving metal-porphyrin complexes, have been reported.[32] (ii) Intramolecular electron transfer between an axially coordinated pyridine molecule and the Fe(III) center (eq 12)[28] followed by the fast scavenging of py$^+$ radical by alcohols (eq 13), in competition with geminate recombination (eq 14).



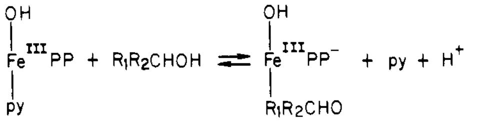
$$^{*}\overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} \longrightarrow \overset{\mathrm{OH}}{\mathrm{Fe^{II}PP^{-}}} + \mathrm{py^+} \tag{12}$$

$$\mathrm{py^+} + \mathrm{R_1R_2CHOH} \rightarrow \mathrm{pyH^+} + \mathrm{R_1R_2\dot{C}OH} \tag{13}$$

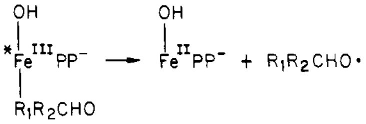


$$\overset{\mathrm{OH}}{\mathrm{Fe^{II}PP^{-}}} + \mathrm{py^+} \longrightarrow \overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} \tag{14}$$

In this case the excited state responsible for the photochemical behavior should be a py → Fe(III) LMCT state. (iii) Intramolecular electron transfer between an axially coordinated alkoxy group and the Fe(III) center (eq 16).



$$\overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} + \mathrm{R_1R_2CHOH} \rightleftarrows \overset{\mathrm{OH}}{\underset{\mathrm{R_1R_2CHO}}{\mathrm{Fe^{III}PP^{-}}}} + \mathrm{py} + \mathrm{H^+} \tag{15}$$

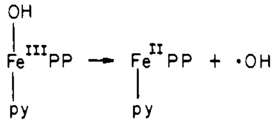


$$^{*}\overset{\mathrm{OH}}{\underset{\mathrm{R_1R_2CHO}}{\mathrm{Fe^{III}PP^{-}}}} \longrightarrow \overset{\mathrm{OH}}{\mathrm{Fe^{II}PP^{-}}} + \mathrm{R_1R_2CHO\cdot} \tag{16}$$

A mechanism of this type was proposed by Groves[33] for the photodissociation of iron(III)–alcohol complexes. In this case scavenging of the alkoxy radicals by alcohol (eq 17)[29] should generate the radicals responsible for the secondary chemistry.

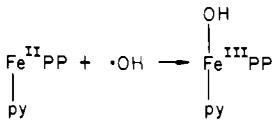
$$\mathrm{R_1R_2CHO\cdot} + \mathrm{R_1R_2CHOH} \rightarrow \mathrm{R_1R_2CHOH} + \mathrm{R_1R_2\dot{C}OH} \tag{17}$$

Although in the experimental conditions used Fe$^{\mathrm{III}}$PP(py)(OH) is thought to be the predominant species,[21] the possibility that axial coordination of alkoxy group trans to OH$^-$ may occur (eq 15) cannot be completely ruled out. In this case the excited state responsible for this behavior should be a R$_1$R$_2$CHO → Fe(III) LMCT state. (iv) Intramolecular electron transfer between the axially coordinated hydroxide ion and the Fe(III) center (eq 18), followed by scavenging ·OH radicals by alcohols (eq 19) in competition with geminate recombination (eq 20).



$$\overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} \longrightarrow \underset{\mathrm{py}}{\mathrm{Fe^{II}PP}} + \cdot\mathrm{OH} \tag{18}$$

$$\cdot\mathrm{OH} + \mathrm{R_1R_2CHOH} \rightarrow \mathrm{R_1R_2\dot{C}OH} + \mathrm{H_2O} \tag{19}$$



$$\underset{\mathrm{py}}{\mathrm{Fe^{II}PP}} + \cdot\mathrm{OH} \longrightarrow \overset{\mathrm{OH}}{\underset{\mathrm{py}}{\mathrm{Fe^{III}PP}}} \tag{20}$$

In this case the excited state responsible for the photochemical behavior should be a OH → Fe(III) LMCT state. Processes of this type are known to occur in hydroxo complexes of Fe(III) upon UV irradiation.[34]

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[28] We thank Professor D. G. Whitten for suggesting this mechanistic possibility.

[29] Alkoxy radicals are known to be powerful oxydants; they are known, however, to produce ketyl radicals in alcohols *via* reactions 10 and 17 with a lifetime of a few microseconds.[30]

[30] Dainton, F. S.; Janovsky, I. V.; Salmon, G. A.; *J. Chem. Soc. D* **1969**, 335.

[31] Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* 1978, 75, 1.

[32] Young, R. C.; Meyer, T. J.; Whitten, D. G.; *J. Am. Chem. Soc.* **1976**, *98*, 286.

[33] Groves, J. T. *Tetrahedron Lett.* **1975**, *36*, 3113 and references therein.

[34] Langford, C. H., Carey, J. *Can. J. Chem.* **1975**, *53*, 2430.

Mechanism i, although possible on energetic grounds if the excited state is a typical porphyrin one,[35] is implausible owing to the presumably very short lifetime of the excited states of iron(III) porphyrin complexes in fluid solution.[4] Moreover, this mechanism is clearly ruled out by the strong wavelength dependence of the quantum yields (Table I), which is at odds with the wavelength-independent behavior of metalloporphyrin luminescence.[4]

As far as mechanisms ii, iii, and iv are concerned, discrimination among the three may prove difficult on experimental grounds. In fact all three require light absorption into specific LMCT bands. All these mechanisms imply dependence on type as well as concentration of the alcohols: mechanism iii through complex formation equilibrium and mechanisms ii and iv through the scavenger content of the solvent cage surrounding the complex (note that the scavenging occurs over an alcohol concentration range much higher than that involved in typical bulk solution scavenging phenomena). The fact that no transient absorbance change can be observed in the absence of alcohols cannot be taken as evidence for mechanism iii since the same result would be expected if the scavenging process of mechanisms ii and iv is to occur in the solvent cage, i.e., in a time scale much shorter than the time resolution of the flash experiments.

As far as the wavelength dependence of the photoreduction quantum yield is concerned, it might be remarked that the photoreduction is only relatively efficient at $\lambda \leq 400$ nm. This implies light absorption into specific electronic absorption bands, which according to mechanisms ii–iv should be of the LMCT type. It can be noticed that the OH → Fe(III) LMCT band in $Fe(H_2O)_5OH^{2+}$ is found at about 300 nm.[34] Considering the lowering in redox potentials obtained in going from the aqueous ion (+0.77 V) to the porphyrin complex (−0.15 V), it might be expected that OH → Fe(III) LMCT bands should lie at wavelengths substantially lower than 300 nm in $Fe^{III}PP(py)(OH)$. Porphyrin complexes containing coordinated alkoxy groups or pyridine (which are more oxidizable than OH^-) would, on the other hand, exhibit R_1R_2CHO → Fe(III) or py → Fe(III) LMCT bands at higher wavelengths. Thus, although no clear-cut decision can be made among mechanisms ii–iv for the primary photoredox process, this argument tends to favor the direct intramolecular electron-transfer mechanism from the coordinated alkoxy group (mechanism iii) or pyridine (mechanism ii) to the metal.[37] The explanation of the much lower primary photoreduction efficiency of *tert*-butyl alcohol relative to the other alcohols (Figure 4) cannot be based on the redox properties of the alcohols (Table II) but rather must involve the low ability of *tert*-butyl alcohol to either coordinate to (mechanism iii) or solvate (mechanism ii) the Fe(III) complex. Figure 1 shows that *tert*-butyl alcohol is by far less effective than the other alcohols in modifying the spectrum of the complex, a feature which supports the above considerations.

As a final comment, it may be noticed that the photochemistry of metal porphyrin complexes is often considered as that of typical porphyrin chromophores, which are modified by the presence of the metal to the extent to which it affects the lifetimes or interconversion efficiencies of the porphyrin excited states. In contrast to this oversimplified view, the results reported in the present paper show that for some metal porphyrin complexes the photochemistry may be entirely determined by specific, high-energy excited states of the whole molecular system.

Acknowledgment. We thank Dr. C. Chiorboli for his kind assistance in performing the gas chromatographic analyses.

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(35) Energies of metalloporphyrin triplet excited states are typically at about 43 kcal/mol (1.87 eV).[4] Given the ground-state redox potential (−0.15 V),[1] it is possible to calculate[31] an excited state reduction potential of about 1.7 V for $Fe^{III}PP(py)(OH)$. In view of the one-electron redox potentials of the alcohols used (Table II) and of pyridine (1.82 V in CH_3CN vs. Ag/Ag^+),[36] the one-electron oxidation of alcohols and pyridine by the excited complex seems to be thermodynamically allowed.

(36) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous systems"; Marcel Dekker: New York, 1970.

(37) While both mechanisms are plausible in this solvent system, it should be noted that qualitatively identical results, i.e., photoreduction of Fe(III) to Fe(II) complex, can be obtained in the absence of pyridine, albeit with poor quantitative reproducibility.

Some Caged Oxyazaphosphoranes

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Abstract: 2,8-Dimethyl-2,5,8-triaza-1-phosphabicyclo[3.3.0]octane (**9**) has been prepared as an extremely unstable monomer. This monomer on standing polymerizes rapidly and reversibly. The monomer has been allowed to react with biacetyl and benzil to give the mixed oxyazaphosphoranes **13** and **14**. Variable-temperature ^{13}C NMR studies show that these materials do not undergo rapid intramolecular ligand reorganization nor do they undergo rapid intermolecular reorganization. In the case of **14** it remains rigid up to 95 °C. 2,10-Dimethyl-2,6,10-triaza-1-phosphabicyclo[4.4.0]decane (**16**) has been prepared and found to be much more stable than **11** toward polymerization. Condensation of **16** with benzil yields a phosphorane, **17**. This material undergoes rapid intramolecular ligand reorganization at room temperature. Variable-temperature ^{13}C NMR studies show that this process has a free energy of activation of 13 kcal/mol with a coalescence temperature of −7 °C. These findings further delineate those factors which control rates of intramolecular ligand reorganization of phosphoranes, and they impose limitations on various proposed mechanisms.

Although the chemistry of phosphoranes has developed rapidly during the past two decades, there are still a number of interesting questions which must be answered before a satisfying understanding of the chemistry of these molecules can be achieved. Some of these questions are as follows: what are the favored structures where the gamut runs from trigonal bipyramidal (TBP) to square or rectangular pyramidal (SP or RP); what factors govern the ligand placement in these structures, i.e., apical (a) or equatorial (e) in a TBP or basal (b) or apical (a) in SP or RP; how do the rates of intramolecular ligand reorganization vary as

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