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Supplementary Material Available: Experimental details including description of disorder problem, positional and anisotropic displacement parameters, bond lengths and angles, and observed and calculated structure-factor amplitudes (61 pages). Ordering information is given on any current masthead page.

Spectral and Electrochemical Identification of Iron(IV)-Oxo Porphyrin and Iron(IV)-Oxo Porphyrin π-Cation Species

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Iron(IV) protoporphyrin IX species have been shown or proposed to play important roles in the mechanisms of peroxidase, cytochrome P-450, and cytochrome oxidase enzymes.[1] Studies focused on the chemical oxidation of iron(III) porphyrins have been designed in order to elucidate structure and reactivities of the higher valent iron porphyrin species. Eminent among these are the studies of Balch[2] and Groves[3] which have dealt with investigations of iron(IV)–oxo porphyrins (peroxidase compound II model) and an investigation of Balch[2c] which provides evidence for an iron(IV)–oxo porphyrin π-cation radical (peroxidase compound I model). Electrochemistry has not been vigorously pursued as a means to both generate and to determine oxidation potentials of iron(IV)–oxo porphyrins and iron(IV)–oxo porphyrin π-cation radicals. We now report the spectral and electrochemical characterization of an electrochemically generated iron(IV)–oxo porphyrin and an iron(IV)–oxo porphyrin π-cation radical.

It is now accepted that the first $1e^-$ oxidation of an iron(III) porphyrin ligated to such anions as Cl^-, ClO_4^-, etc. is porphyrin centered resulting in the formation of an iron(III) porphyrin π-cation radical. Further $1e^-$ oxidation leads to an iron(III) porphyrin dication.[5] These electrochemical studies did not include strongly basic oxyanions as ligands due to the problem of μ-oxo-dimer formation. We have examined the electrochemistry of sterically hindered porphinato iron(III) hydroxide and methoxide salts and have demonstrated that the ligation of strongly basic oxy ligands results in a new peak. The presence of this new peak (about 100 mV less positive than the first oxidation for the chloride salt of the corresponding iron(III) porphyrin) was taken as the first evidence for the room-temperature existence of iron(IV)–oxo species; however, this species is only stable at ambient temperatures on the cyclic voltammetric time scale (scan rate = 25–400 mV/s).[4]

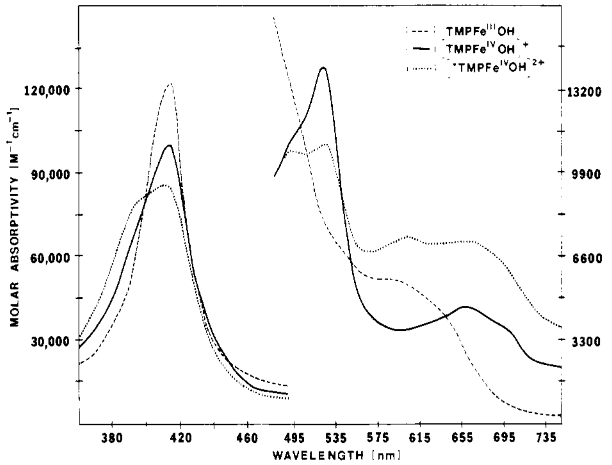

Figure 1. Visible spectra (at −78 °C) of the *meso*-tetrakis[(2,4,6-trimethylphenyl)porphinato]iron(IV) hydroxide species ($[(\mathrm{TMP})\mathrm{Fe^{IV}OH}]^+$) formed by $1e^-$ oxidation of $(\mathrm{TMP})\mathrm{Fe^{III}OH}$ and the corresponding iron(IV) hydroxy porphyrin π-cation radical ($[\cdot(\mathrm{TMP})\mathrm{Fe^{IV}OH}]^{2+}$) formed by $1e^-$ oxidation of ($[\mathrm{TMPFe^{IV}OH}]^+$) in 5% CH_3OH/CH_2Cl_2 (with 0.1 M tetrabutylammonium perchlorate). From repetitive spectral scanning isosbestic points for oxidation of $\mathrm{TMPFe^{III}OH}$ to $[\mathrm{TMPFe^{IV}OH}]^+$ were determined to be at 405, 425, 502, and 550 nm while the maximum absorbances of the latter are found at 415 (Soret band) and 525 nm. For $[\cdot(\mathrm{TMP})\mathrm{Fe^{IV}OH}]^{2+}$ isosbestic points are at 400, 426, 485, and 545 nm while maximum absorbances of the latter are found at 398, 412, 600, and 670 nm. With the exception of a small bathochromic shift of approximately 5 nm in the α,β region, the spectrum shown in this figure are unaltered on transfer to Burdick and Jackson dichloromethane solvent.

In order to observe the iron(IV)–oxo porphyrin products of the electrochemical oxidation a special 1.0-mm spectroelectrochemical quartz cuvette was designed with a gold minigrid (10^3 lines/in.^{2}) working electrode; in quartz side compartments fused to the cuvette a platinum flag auxiliary electrode (separated from the cuvette by a medium glass frit) and an Ag/AgCl reference electrode (filled with aqueous tetramethylammonium chloride, adjusted to 0.00 V vs. saturated calomel electrode) were mounted. The entire apparatus was maintained at −78 °C. For the purpose of the present study *meso*-tetrakis[(2,4,6-trimethylphenyl)porphinato]iron(III) hydroxide [$(\mathrm{TMP})\mathrm{Fe^{III}OH}$] was used as the representative iron(III) porphyrin. The solvent employed was CH_2Cl_2 (Burdick and Jackson). Potentials for consecutive $1e^-$ oxidation of $(\mathrm{TMP})\mathrm{Fe^{III}OH}$ were determined by conventional CV at −78 °C. Oxidation products were generated in the spectroelectrochemical cuvette by $1e^-$ and $2e^-$ controlled-potential electrolysis at the required potentials. Constant monitoring of the visible spectra was carried out during the course of the electrochemical oxidations. In Figure 1 there are presented the visible spectra of $(\mathrm{TMP})\mathrm{Fe^{III}OH}$ and its 1- and $2e^-$ oxidation products. Examination of Figure 1 shows that the first $1e^-$ oxidation (1.05 V vs. SCE) results in a decrease in absorbance of the Soret band (415 nm) without a change in its position and a new absorption peak appears at 520 nm. The latter is not associated with the starting $(\mathrm{TMP})\mathrm{Fe^{III}OH}$ nor to the eventual decomposition product [$(\mathrm{TMP})\mathrm{Fe^{III}Cl}$] of the electrochemical reaction. The π-cation radical of $(\mathrm{TMP})\mathrm{Fe^{III}Cl}$ also displays an absorbance around 520 nm; on the other hand the most characteristic feature for the visible spectrum of a π-cation radical is the shift of the Soret band to below 400 nm.[3] This is clearly not observed during the $1e^-$ oxidation of $(\mathrm{TMP})\mathrm{Fe^{III}OH}$. Additional evidence that the product is $[(\mathrm{TMP})\mathrm{Fe^{IV}OH}]^+$ was obtained by the addition of 1 equiv of 1-methylimidazole which brought about a shift of the 520-nm peak to 570 nm, which is consistent with Balch's report of an absorbance at 560 nm (toluene) of iron(IV) *meso*-tetraphenylporphyrin ligated to 1-methylimidazole.[2b] The λ_{max} values of $[(\mathrm{TMP})\mathrm{Fe^{IV}OH}]^+$ and $[(\mathrm{TMP})\mathrm{Fe^{IV}OCH_3}]^+$ in 5% CH_3OH/CH_2Cl_2 (v/v) are at 525 nm. On addition of 1 equiv of CH_3O^- to the electrochemically

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generated $[(TMP)Fe^{IV}OCH_3]^+$ a species is formed with a Soret band at 423 nm, a major peak at 540 nm, and a minor peak at 575 nm. This spectrum is essentially identical with a spectrum reported by Groves[3a] (5% CH_3OH/CH_2Cl_2) who proposed the structure $(TMP)Fe^{IV}(OCH_3)_2$.

Means for generating (porphinato)iron(IV)–oxo π-cation radical species in order to determine their spectral characteristics have not been available. It is this oxidation state that is of primary concern to those interested in the reactions of cytochrome P-450. The controlled-potential 1e⁻ oxidation of $[(TMP)Fe^{IV}OH]^+$ was carried out at 1.22 V (vs. SCE). This is accompanied by a slight blue shift in the Soret band and a decrease in its molar absorptivity as an absorbance peak develops at 398 nm which is very diagnostic of a π-cation radical. The broad secondary absorbance peaks (605, 670 nm) are also diagnostic of a π-cation radical (Figure 1). The cyclic voltammogram of the product ($[\cdot(TMP)Fe^{IV}OH]^{2+}$) establishes that it has been formed from an iron(III) species by two reversible 1e⁻ oxidation steps.

In conclusion, $(TMP)Fe^{III}OH$ undergoes two reversible 1e⁻ oxidations. The first oxidation step must be metal-centered because it is not accompanied by a blue shift in the Soret band and the spectrum of the product is quite similar to those reported previously for iron(IV) porphyrins. The visible spectrum of the product formed in the second 1e⁻ oxidation step clearly supports the conclusion that a π-cation radical is being formed. This can be summarized in eq 1 and 2. The conclusion[2-4] that ligation

$$(TMP)Fe^{III}OH \rightarrow [(TMP)Fe^{IV}OH]^+ + e^- \qquad E = 1.01\ \text{mV} \tag{1}$$

$$[(TMP)Fe^{IV}OH]^+ \rightarrow [\cdot(TMP)Fe^{IV}OH]^{2+} + e^- \qquad E = 1.14\ \text{mV} \tag{2}$$

of a strongly basic oxyanion to an iron porphyrin results in metal-centered oxidation being favored over porphyrin-centered oxidation is borne out by these spectral and electrochemical investigations. Further extension of these observations are current being pursued by this laboratory.

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Photocatalysis of Oxygen Transfer from *p*-Cyano-*N*,*N*-dimethylaniline *N*-Oxide to *meso*-(Tetraphenylporphinato)chromium(III) Chloride

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In recent studies we have shown that *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide (NO) transfers oxygen to the metal centers of iron(III) and manganese(III) tetraphenylporphyrins to yield higher valent oxoiron and oxomanganese porphyrin species plus *p*-cyano-*N*,*N*-dimethylaniline (DA).[1] In the interim, Murray and Sligar[2] have reported results of a model study of cytochrome $P\text{-}450_{scc}$ based upon the quantitative oxidation of 1-phenyl-1,2-ethanediol (PED) by NO in the presence of *meso*-(tetraphenylporphinato)chromium(III) chloride [$(TPP)Cr^{III}Cl$] as catalyst to yield benzaldehyde and DA.[3] At the same time we defined the relationships between $(TPP)Cr^{III}Cl$ and the oxo-complexes $(TPP)(Cl)Cr^{V}O$ and $(TPP)Cr^{IV}O$ and reported that oxygen transfer from NO to $TPPCr^{III}Cl$ requires photoexcitation.[3] We report herein preliminary studies which show that the oxochromium species proposed as the reactive oxidant for PED oxidation[2] is most likely $(TPP)(Cl)Cr^{V}O$ and that the rate of reaction reported by Murray and Sligar was severely limited by an absence of specific photocatalytic activation.

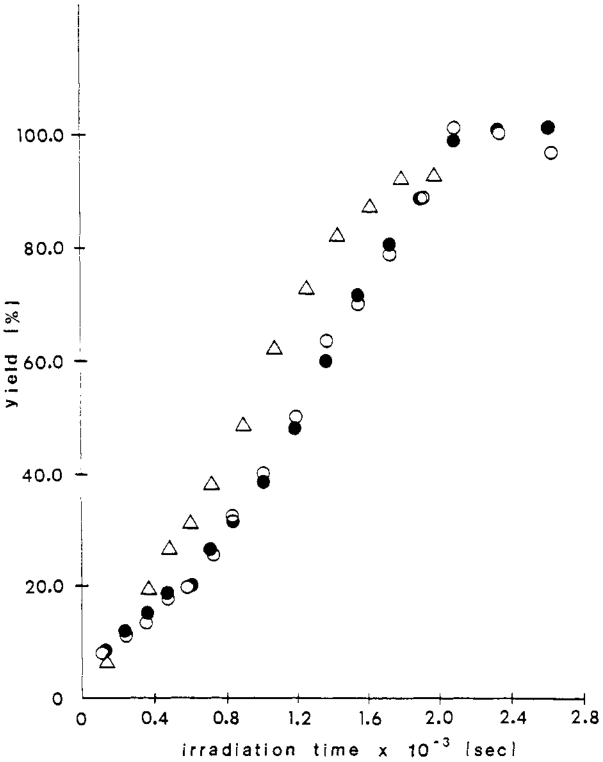

Figure 1. Plots of yields of benzaldehyde (●) and DA (○) vs. irradiation time: (A) [PED] = 3.0 × 10^{-2} M, [NO] = 1.2 × 10^{-3} M, and [$(TPP)Cr^{III}Cl$] = 1.0 × 10^{-4} M in CH_3CN at room temperature. (B) same as plot (A), but including DA at 1.2 × 10^{-3} M and analyzing for benzaldehyde with time (△).

That oxygen transfer from the *N*-oxide to chromium(III) porphyrin requires photocatalysis is shown by the following experiment. The visible absorbance, monitored with time at the λ_{max} of $(TPP)Cr^{IV}O$ (429 nm), was found to be unchanged over an 18-h period when an acetonitrile solution containing $(TPP)Cr^{III}Cl$ (1.0 × 10^{-4} M)[4] and NO (1.2 × 10^{-3} M) was maintained in the dark. Irradiation by diffuse room fluorescent light for only 2 min resulted in a change of the green color of $(TPP)Cr^{III}Cl$ to orange. The spectrum of the spent reaction solution exhibited a broad absorption with maxima at 426 and 412 nm characteristic of a mixture of $(TPP)Cr^{IV}O$ and $(TPP)(Cl)Cr^{V}O$.[5] Transfer of the reaction from acetonitrile to dichloromethane provided similar results and from the spectrum it could be estimated that $(TPP)Cr^{IV}O$ was formed in a 95% yield. Since the photocatalysis results in a very rapid reaction with reactants at low concentrations when the light source is meager it appears obvious that the quantum yield must be much greater than 1.0. From this it follows that oxygen transfer from NO to $(TPP)Cr^{III}Cl$ should be anticipated as a photoinitiated chain reaction.

In the $(TPP)Cr^{III}Cl$ photocatalyzed oxidation of PED with NO the final products are benzaldehyde, formaldehyde, DA, and $(TPP)Cr^{III}Cl$ (plus less than 1% *p*-cyano-*N*-methylaniline formed upon demethylation of DA). The autocatalytic nature of this reaction is shown by the following experiment. Five milliliters of a CH_3CN solution containing PED (3.0 × 10^{-2} M), NO (1.2 × 10^{-3} M), and $(TPP)Cr^{III}Cl$ (1.0 × 10^{-4} M) under N_2 was

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