the sample container. Reduction of the cyclophane was carried out by tilting the container, so that the solution was poured onto the finely dispersed compound in a precooled narrow ESR sample tube. All operations were performed in vacuo at 168 K (coolant, hexane with liquid nitrogen).

Radical Anions of 2 and Its Deuterio Derivative. The chemical method of preparation implied a reaction of the compound with potassium mirror in DME. The electrolytic reduction made use of a cylindric cell containing a helical cathode of amalgamated gold and a platinum wire anode along the axis;[36] the solvent and supporting salt were *N*,*N*-dimethylformamide and Et_4NClO_4, respectively.

Instrumental. The equipment for cyclic voltammetry was a Metrohm-Polarecord E56 (VA Scanner 612/VA Stand 663). The ESR spectra were taken on a Varian-E9-instrument, while a Bruker-ESP 300 spectrometer system served for the ENDOR and TRIPLE resonance studies.

Acknowledgment. We thank Professor Virgil Boekelheide for samples of **1** and **2**, Dr. Hiroaki Ohya-Nishiguchi for performing some preliminary experiments, Mr. U. Buser for synthesizing para-D_8-**2**, and Dr. Claudine Cohen-Addad for communicating the X-ray crystallographic data of **1** prior to publication. The Swiss National Science Foundation is gratefully acknowledged for financial support.

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Identification of High-Valent Fluoroiron Porphyrin Intermediates Associated with the Electrocatalytic Functionalization of Hydrocarbons

David L. Hickman, Alaganandan Nanthakumar, and Harold M. Goff*

Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52242.

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Abstract: The difluoroiron(III) tetraphenylporphyrin complex undergoes a one-electron oxidation at 0.68 V (SCE) in contrast with values of 1.1 V measured for the monofluoroiron(III) porphyrin and the other five-coordinate iron(III) porphyrin complexes. Cyclic voltammetric oxidation of the difluoroiron(III) species in dichloromethane solution is quasi-reversible as a consequence of an EC mechanism. Reversible waves are favored at high scan rates and lower temperatures. Increased water content serves to make the oxidative cyclic voltammetric process irreversible presumably due to a disproportionation process. In the presence of added olefin substrates, this EC process permits efficient electrocatalytic oxidation to the epoxide, allylic alcohol, and enone. Tertiary carbon units are converted to the corresponding alcohol. Utilization of fluoride ion permits generation and low-temperature spectroscopic identification of a highly oxidized iron porphyrin species. The high-valent complex is produced at −78 °C through addition of *m*-chloroperbenzoic acid to monofluoroiron(III) tetraarylporphyrins or by fluoride ion promoted disproportionation of the dication radical μ-oxo dimeric iron(III) porphyrin derivative. The oxidized iron porphyrin species is competent to effect olefin epoxidation at −78 °C. Low-temperature ^1H and ^2H NMR spectroscopies demonstrate the porphyrin π-cation radical nature of the high-valent species, in that porphyrin phenyl resonances are drastically shifted in alternating upfield and downfield directions. The electron spin resonance spectrum is consistent with an $S = {}^3/_2$ ground state, and the high-valent intermediate is assigned a tentative fluorooxoiron(IV) porphyrin π-cation radical formulation.

High-valent iron oxo porphyrin species are proposed as intermediates in the reaction cycles of the peroxidases,[1] catalases,[1] cytochrome P-450,[2] and cytochrome oxidase.[3] Generation of such high-valent, isolated synthetic metalloporphyrin derivatives is of interest in terms of biomimetic studies and as a possible route to development of oxidative catalytic systems. Oxidation of metalloporphyrins may be ring-centered or metal-centered, meaning that the electron(s) may be removed from a molecular orbital that is centered predominantly either on the porphyrin ring or on the metal ion. One-electron oxidation of most simple five-coordinate high-spin iron(III) porphyrins has been shown to produce the corresponding iron(III) porphyrin π-cation radical species.[4] Recent evidence has been offered for metal-centered oxidation of hydroxide, methoxide, and aryl-ligated iron(III) porphyrins.[5] Metal-centered oxidation to the iron(IV) state (detectable at low temperature) is certainly dictated by a very basic oxo ligand[6] or two axial methoxide ligands.[7] Two-electron oxidation of the iron(III) porphyrin by oxo-transfer reagents seemingly yields an oxoiron(IV) porphyrin cation radical species[6c,8] analogous in electronic structure to the compound I state of peroxidases.

Binding of basic, "hard" axial ligands is expected to stabilize metal-centered oxidation, and in this regard fluoride coordination

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appeared to provide a potential route for generation of iron(IV) porphyrin complexes. It has been known for some time that two fluoride ions will bind to iron(III) porphyrins in aprotic solvents to form the six-coordinate high-spin complex.[9] Further characterization of this difluoroiron(III) porphyrin adduct led to the realization that the first cyclic voltammetric oxidation wave was shifted approximately 0.4 V negative with respect to the monofluoroiron(III) analogue.[10] The redox chemistry of the difluoroiron(III) porphyrin complex is complicated by the fact that cyclic voltammetric waves are irreversible at slow scan rates, suggestive of an EC (electrode-chemical) mechanism. Hence, the single-electron oxidation product of difluoroiron(III) porphyrins undergoes a secondary reaction with solvent, supporting electrolyte, and/or small amounts of water to ultimately yield the parent difluoroiron(III) porphyrin species. The preliminary application of this oxidative electrochemical catalysis has been reported for cyclohexene oxidation to mixtures of the epoxide, enol, and enone.[10] This report describes further characterization of the electrochemical process, reaction pathways, and low-temperature identification of the putative active oxidizing species.

Experimental Section

Solvents. Chlorinated solvents were purified by concentrated H_2SO_4 washes (until the H_2SO_4 came through colorless), followed by two water washes, two aqueous 10% Na_2CO_3 washes, and two more water washes. After they were dried over calcium chloride, the solvents were distilled from P_4O_{10} into brown bottles containing activated 4-Å molecular sieves. Acetonitrile, benzene, and acetone were purified by modifications of published methods.[11]

Iron Porphyrins. Tetraphenylporphyrin ($TPPH_2$), tetrakis(*p*-methoxyphenyl)porphyrin (*p*-$OMeTPPH_2$), and tetra-*p*-tolylporphyrin ($TTPH_2$) were prepared by the standard pyrrole–aryl aldehyde condensation reaction.[12] Tetramesitylporphyrin ($TMPH_2$) was prepared by a sealed-tube reaction.[13] Specifically deuteriated iron(III) tetraphenylporphyrins were prepared as previously described.[14] Iron incorporation was effected by addition of a 10-fold excess of solid anhydrous $FeCl_2$ to a DMF solution of the porphyrin at reflux under a nitrogen atmosphere.[15] The iron porphyrin product was recovered from the cool DMF solution by addition of an aqueous sodium chloride solution. The resulting iron(III) porphyrin dissolved in dichloromethane was converted to the μ-oxo dimeric state by equilibration with aqueous sodium hydroxide solution. Purification was effected by silica gel chromatography, and the integrity of the final μ-oxo dimeric species was ensured by passage of the dichloromethane solution through a short basic alumina (Fisher, A-941) column. The chloride and fluoride complexes were produced by equilibration of the appropriate μ-oxo dimer solution with aqueous 1 M HCl or HF (in a Teflon container). The crystalline five-coordinate haloiron(III) porphyrin products were isolated by concentration of the dichloromethane solution with addition of heptane.

Two-electron oxidation of the μ-oxo dimeric compound $[(TPP)Fe]_2O$ was carried out by electrochemical methods as previously described.[4d,16] The $[(TPP)Fe]_2(ClO_4)_2$ product was isolated in crystalline form by addition of acetone to the electrolyzed solution. The one-electron oxidation product, (*p*-OMeTPP)Fe(Cl)(ClO_4), was prepared by electrochemical oxidation and isolated from the supporting electrolyte by selective solvent extraction.[4d]

Electrochemical Techniques. Tetraalkylammonium salts utilized as supporting electrolytes (Bu_4NClO_4 and Pr_4NClO_4) were purified by recrystallization from 1:4 acetonitrile/water followed by a vacuum drying step over P_4O_{10}. Tetrabutylammonium fluoride trihydrate and anhydrous Bu_4NF on silica gel were purchased from Alfa. Electrochemical oxidations were performed with a three-electrode cell configuration that employed a Princeton Applied Research (PAR) Model 173 potentiostat. Supporting electrolyte concentrations were 0.1 M, and iron porphyrin concentrations were 1.0–1.5 mM. Counter electrodes and reference electrodes consisted of silver wires immersed in 0.1 M supporting electrolyte solutions in separate tubes fitted with very fine glass frits. The PAR Model 173 potentiostat and Model 175 universal programmer were used for cyclic voltammetric measurements. The reference electrode for cyclic voltammetry measurements consisted of a silver wire immersed in a 0.1 M $AgNO_3$/acetonitrile solution separated from the bulk solution by porous Vycor glass. A platinum bead and platinum coil were used as the working and counter electrodes, respectively. Potentials were adjusted to the conventional aqueous SCE reference by application of a factor of 0.38 V. This conversion factor was determined by comparison of apparent potentials for iron porphyrins (1 mM) dissolved in dichloromethane (0.1 M tetrabutylammonium perchlorate) that employed, in separate experiments, the PAR aqueous SCE electrode and the PAR Ag/0.10 M $AgNO_3$/acetonitrile electrode. Significant junction potentials are ignored in referencing the aqueous SCE electrode for apolar organic solvents.[17] For purposes of using ferrocene to correct for junction potentials, it should be noted that the first oxidation potential of $(TPP)FeF_2^-$ is 0.16 V positive of ferrocene oxidation and 0.68 V positive of the SCE.

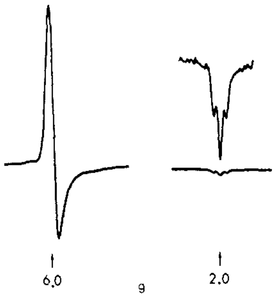

Figure 1. Electron spin resonance spectrum of (*p*-$OCH_3TPP)FeF_2^-$ in 1/1 dichloromethane/toluene at −180 °C, 1 mM iron porphyrin, and 10 mM $Bu_4NF{\cdot}3H_2O$.

Instrumental Techniques. Gas chromatograms were obtained on a Varian Model 3700 gas chromatograph, generally with 1-μL injections, at a flow rate of 30 mL/min, an injector temperature of 270 °C, and an initial column temperature of 50 °C. An OV-101 silica gel column was employed. Gas chromatography/mass spectral data was obtained from a Hewlett Packard 5985B GC-MS.

^1H and ^2H NMR measurements were carried out at 360 and 55 MHz, respectively, on a Bruker WM-360 pulsed FT spectrometer. Solutions contained 1.0–5.0 mM iron porphyrin. Temperature calibration was performed by use of the Van Geet thermometer.[18] Low-temperature measurements on unstable materials were made by cooling the iron porphyrin solution contained in the NMR or EPR tube in dry ice, followed by addition of the $Bu_4NF{\cdot}3H_2O$ or *m*-chloroperbenzoic acid (MCPBA) solution slowly down the side of the cold tube with subsequent rapid mixing.

Electron paramagnetic resonance spectra were recorded on a Varian E-104A spectrometer equipped with an Air Products cryostat at liquid-nitrogen or liquid-helium temperatures as indicated.

Results

Difluoroiron(III) Porphyrin Complex Formation. Solution preparation and physiochemical studies of difluoroiron(III) porphyrin complexes have received emphasis in an earlier report,[10] and previously described results will only be summarized here. Addition of hydrated tetrabutylammonium fluoride ($Bu_4NF{\cdot}3H_2O$) to a dichloromethane solution of (TPP)FeF results in generation of the difluoro complex. The equilibrium constant for this process is 4×10^3 M^{-1} at 25 °C. It should be noted that use of chloroform results in an apparent binding constant that is orders of magnitude less favorable as a likely consequence of fluoride–chloroform hydrogen bonding.[10]

The difluoroiron(III) porphyrin complex remains in the high-spin state as is evident by a solution magnetic susceptibility value

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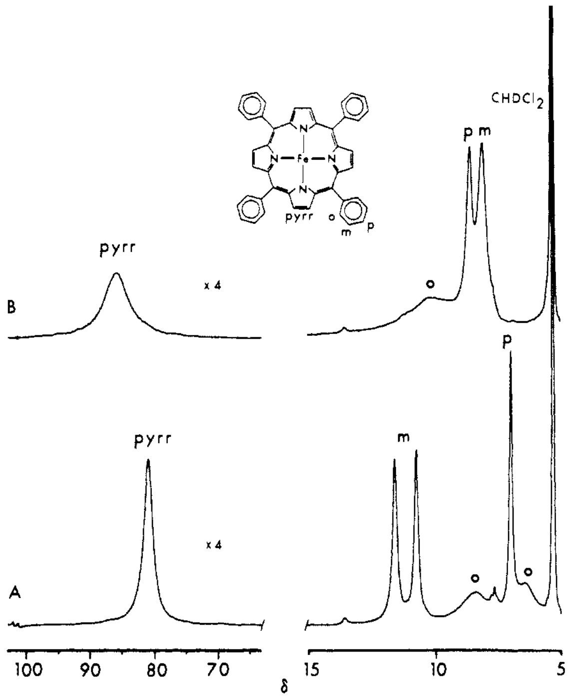

Figure 2. Downfield region of ^{1}H NMR spectra at 25 °C with CD_2Cl_2 as solvent and chemical shifts referenced to $(CH_3)_4Si$ for (A) (TPP)FeF and (B) $(TPP)FeF_2^-$ containing 10 mM $Bu_4NF{\cdot}3H_2O$.

of 6.0 ± 0.2 μ_B in dichloromethane solution at 308 K.[10] The EPR spectra for both the monofluoro and difluoro complexes were typical for high-spin iron(III) species with strong $g = 6$ and weak $g = 2$ signals. In an earlier report it was noted that no fluorine hyperfine structure was apparent for the $g = 2$ signal of $(TPP)FeF_2^-$ in dichloromethane at 80 K.[9b] However, our more recent measurements show that, at 5 K in a 1:1 toluene/dichloromethane glass, the $g = 2$ signal for (TPP)FeF is split into a doublet with a coupling constant of 45 G, and at temperatures as high as 93 K the $(TPP)FeF_2^-$ or $(p\text{-OMeTPP})FeF_2^-$ complex (EPR spectrum in Figure 1) produces a triplet with a 36-G coupling constant. The equivalence and coordination of the two fluoride ions is thus illustrated for $(TPP)FeF_2^-$, as was previously demonstrated by EPR spectroscopy for difluorodeuterohemin dimethyl ester.[9a]

^{1}H NMR spectra for (TPP)FeF and $(TPP)FeF_2^-$ are compared in Figure 2. The far downfield pyrrole proton signal is typical for high-spin (TPP)Fe^{III} adducts. The decidedly greater line width for the $(TPP)FeF_2^-$ pyrrole signal as compared with that for (TPP)FeF is suggestive of a smaller zero-field splitting value for the doubly ligated adduct. Shift of the pyrrole signal to 85.8 ppm is also noteworthy, as this signal is found in the 75–80 ppm region for most five-coordinate complexes, and at 72 ppm for the bis(dimethyl sulfoxide) complex.[19,20] Utilization of phenyl-substituted tetraarylporphyrin analogous permitted assignment of the phenyl ^{1}H NMR signals of $(TPP)FeF_2^-$. Splitting of the *o*- and *m*-phenyl proton signals in (TPP)FeF is associated with a five-coordinate iron structure and absence of a plane of symmetry in the porphyrin ring. Corresponding lack of splitting in the *o*- and *m*-phenyl signals of $(TPP)FeF_2^-$ supports the assumption of diaxial fluoride coordination.

Cyclic Voltammetric Studies. The first-oxidation potential of the iron(III) porphyrin complex is drastically affected by addition of the second fluoride ion. The cleanly reversible cyclic voltammetric wave for (TPP)FeF is observed at 1.09 v,[4a] whereas the $(TPP)FeF_2^-$ adduct exhibits a wave at 0.68 V that becomes irreversible at slow scan speeds.[10] The current response as a function of scan rate is described in Figure 3. An EC process is suggested in which the oxidized product, $(TPP)FeF_2$, reacts with dichloromethane solvent, the tetraalkylammonium ion, or the trace water introduced with the hydrated fluoride salt. Any changes in potential due to the EC mechanism were not detectable over a sweep range of 50–1000 mV/s due to the uncertainties attributable to *IR* losses in a resistive solvent such as dichloromethane. A role for water in this process was clearly indicated by experiments in which water was added to the dichloromethane solution of $(TPP)FeF_2^-$, $Bu_4NF{\cdot}3H_2O$, and Pr_4NClO_4. The added water introduces background current at high potentials, but most importantly the reverse wave that would correspond to reduction of the $(TPP)FeF_2$ species is nearly lost when dichloromethane is water-saturated. For example, at a scan rate of 200 mV/s the i_{pa}/i_{pc} ratio increased from approximately 6 to 18 upon saturation of the electrolyte–dichloromethane solution with water.

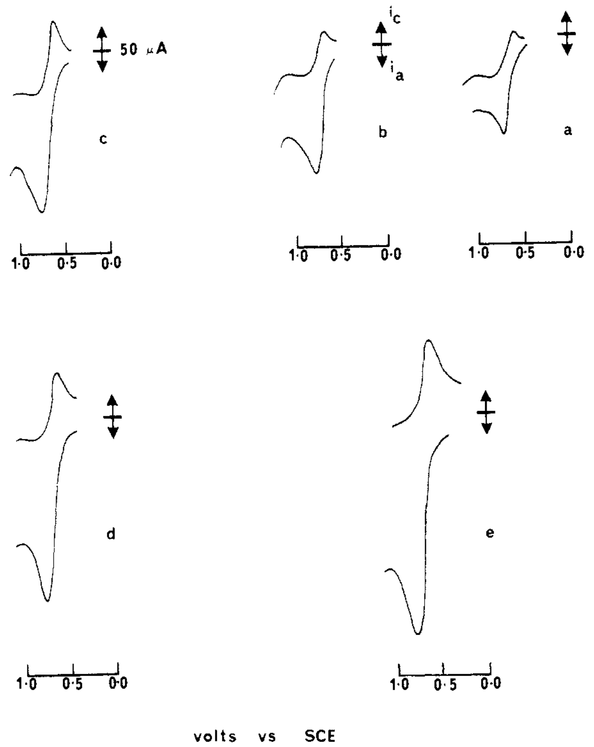

Figure 3. Effect of scan rate on the ratio of the peak currents (measured from the zero-current base-line level) of the anodic (i_{pa}) and cathodic (i_{pc}) cyclic voltammetric waves of $(TPP)FeF_2^-$: dichloromethane solvent, 0.10 M Pr_4NClO_4, 2.5 mM $Bu_4NF{\cdot}3H_2O$, 1.0 mM (TPP)FeF. Potentials are adjusted to the SCE reference: (a) 50 mV/s, $i_{pa}/i_{pc} = 8.3$; (b) 100 mV/s, $i_{pa}/i_{pc} = 7.0$; (c) 200 mV/s, $i_{pa}/i_{pc} = 5.2$; (d) 500 mV/s, $i_{pa}/i_{pc} = 3.6$; (e) 1 V/s, $i_{pa}/i_{pc} = 2.9$.

An increase in the reversible nature of the CV profiles was observed upon cooling the solution. The i_{pa}/i_{pc} ratio decreased from 12 to 6 when the temperature was lowered from +25 to −10 °C at a scan rate of 100 mV/s and 4.5 mM concentration of the fluoride salt. The increase in cathodic current was more readily apparent at lower scan rates. Hence, the EC process is suppressed, and the direct oxidation product, $(TPP)FeF_2$, is stabilized at the reduced temperature. When the solution was returned to room temperature the anodic to cathodic peak current ratio returned to the original value.

Figure 4 reveals the appearance of a new reduction wave at −0.12 V when more rapid scan rates (500 mV/s) are employed. This wave does not correspond to the difluoroiron(III) to iron(II) reduction that is reported at −1.10 V.[9c] The new wave is barely detectable when the positive scan is carried to 1.1 V but is greatly enhanced for a scan carried to 1.4 V or for a scan that was initiated at +1.0 V in a negative direction after a delay of 45 s. The new wave is seemingly the reductive component for one of the products of the EC process associated with oxidation of $(TPP)FeF_2^-$. The intensity of this wave was greatly diminished at −10 °C (scan not shown). The −0.12-V wave was not present in the absence of iron porphyrin.

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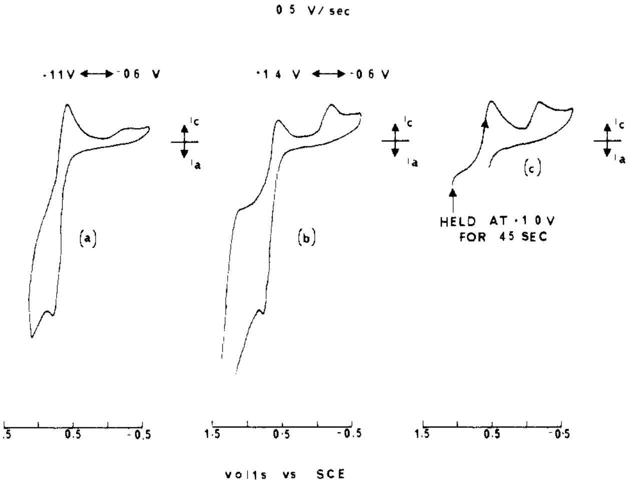

Figure 4. Appearance of a new reductive wave at rapid scan rates and with preapplication of positive potentials: dichloromethane solvent, 0.10 M Pr_4NClO_4, 4.0 mM $Bu_4NF{\cdot}3H_2O$, 1.0 mM (TPP)FeF, potentials adjusted to the SCE reference. (a) The potential was cycled between +1.1 and −0.6 V beginning at +0.38 V. (b) The potential was cycled between +1.4 and −0.6 V beginning at 0.38 V. (c) The potential was held at +1.0 V for 45 s prior to the negative scan.

At scan rates lower than 10 mV/s, the shape of the CV profile for the oxidation of $(TPP)FeF_2^-$ indicates the overlap of two anodic waves. At these low scan rates the addition of 10% cyclohexene results in a lowering of anodic current and a more nearly reversible CV profile. A similar gain in reversibility at low scan rates was observed when the solution was cooled to −10 °C in the absence of cyclohexene.

Electrocatalysis. The apparent existence of an EC mechanism for oxidative electrolysis of 1.0 mM $(TPP)FeF_2^-$ in dichloromethane containing 0.10 M Pr_4NClO_4 (or Bu_4NClO_4) and 10 mM $Bu_4NF{\cdot}3H_2O$ suggested that the transient, electrochemically generated species could be utilized to effect the functionalization of organic substrates. Alkenes and alkanes were accordingly evaluated as possible substrates for capture of the transient oxidizing equivalents generated by electrochemical oxidation of $(TPP)FeF_2^-$. Cyclohexene was investigated in the greatest detail. For this purpose, dichloromethane solutions containing 10% cyclohexene, $(TPP)FeF_2^-$ (1 mM, generated from (TPP)FeF and 10 mM $Bu_4NF{\cdot}3H_2O$), and Bu_4NClO_4 (0.10 M) were electrolyzed at potentials slightly positive of the observed oxidation wave through use of a 1-cm-diameter platinum-basket working electrode. Separate counter and reference electrodes consisted of silver wires placed in 0.10 M Bu_4NClO_4 dichloromethane solutions that were separated from the bulk medium by very fine glass frits. Electrolyses were typically carried out with N_2 agitation of 15 mL of solution for a period of 1 h. The current would remain relatively constant, near 10 mA during most of this time, and would then drop sharply to approximately 1 mA.

Following electrolysis, volatile components were separated from supporting electrolyte, excess fluoride salt, and iron porphyrin by flash vacuum distillation. The volatile mixture was analyzed by gas chromatography and gas chromatography/mass spectrometry. With cyclohexene as substrate, the principal oxidation products were found to be cyclohexenone, 2-cyclohexen-1-ol, and cyclohexene oxide. These products were found in approximately equimolar ratios, even for initial electrolysis periods of only 5 min. Use of *cis*-stilbene as a substrate yielded *cis*-stilbene epoxide and no detectable *trans*-epoxide. *trans*-Stilbene was unreactive in the electrolysis in that no oxidized stilbene products were detected under the solution conditions noted above for cyclohexene. Under these experimental conditions no oxidized products were detected when cyclohexane was employed as a test substrate. However, hydroxylation at the tertiary carbon position was demonstrated for 2,2,4-trimethylpentane, in which cas GC/MS analysis revealed production of the tertiary alcohol.

Various control and blank experiments were performed. No oxidized cyclohexene products were detected if either the monofluoroiron(III) prophyrin or the fluoride salt was excluded from the solution. Likewise, the oxidized products were not detected if the applied potential was lower than the first oxidation wave of $(TPP)FeF_2^-$. Electrolysis at a potential some 0.5 V above the first oxidation wave for $(TPP)FeF_2^-$ resulted in greatly diminished yields of oxidized cyclohexene products. Water introduced from the hydrated fluoride salt (>3 mol of water/mol of fluoride ion) apparently provides a source of oxygen. Attempts were made to investigate the electrolytic process under "dry" conditions. However, efforts to solubilize an anhydrous form of fluoride ion from anhydrous Bu_4NF on silica gel (Alfa) were unsuccessful, as insufficient fluoride ion was dissolved in dichloromethane to effect generation of the difluoroiron(III) porphyrin complex.

Determination of the efficiency of the electrocatalytic system by difference coulometric measurements was unreliable due to the relative magnitude of the background current. Comparison of GC traces for standard solutions of authentic cyclohexene epoxide, 2-cyclohexenone, and 2-cyclohexen-1-ol to the traces for the electrolyzed solutions revealed a turnover number for the (TPP)Fe complex of greater than 25 (turnover = 2[(2 mol of enone + mol of epoxide + mol of cyclohexenol)/mol of (TPP)Fe]. This yield approximates the theoretical value associated with a current of 10 mA for 1 h. Hence, the electrochemical efficiency of the system is quite favorable. A 25-fold turnover with respect to the 1.0 mM iron porphyrin would represent consumption of approximately 40% of the water associated with 10 mM $Bu_4NF{\cdot}3H_2O$. After an electrolysis in which the current had dropped to 10% of the initial value, optical spectra revealed that the principal iron porphyrin species was that of the parent monofluoro complex, (TPP)FeF. Hence, as water is consumed in the olefin oxygenation reactions, acid is produced that presumably is incorporated into the stable bifluoride ion. The excess fluoride ion necessary for formation of the difluoro complex is removed as the bifluoride ion, and the electrocatalytic system no longer functions. Greater than 90% of the iron porphyrin is recovered unchanged after a 1-h electrolysis.

Even though an electrocatalytic scheme is proposed for olefin oxidation, addition of cyclohexene had no apparent effect on the variable-rate cyclic voltammetry profiles at rates greater than 20 mV/s. Thus, the ratio of cathodic to anodic currents for the 0.68-V wave decreased progressively at slower scan rates, and no catalytic wave was seen with addition of 10% cyclohexene. This observation is understandable in view of the more complex EC mechanism proposed below in which disproportionation and hydrolysis reactions are required to produce the reactive oxidizing agent. Cyclohexene presumably does not react with the initially oxidized $(TPP)FeF_2$ species, and hence substrate addition has no effect on the CV profile at high scan rates.

Use of the radical trap diphenylpicrylhydrazyl at 11 mM completely blocked oxidation of cyclohexene. This competition reaction with radical-trapping agents is also seen for in vitro cytochrome P-450 reactions.[21] Addition of Proton Sponge (1,8-bis(dimethylamino)naphthalene) at 60 mM in an attempt to neutralize acid produced in the oxidation reactions also resulted in no production of cyclohexene oxidation products. Use of Proton Sponge as a hindered base to prevent fluoride ion conversion to the bifluoride ion may have been an unfortunate choice, in that the functionalized naphthalene may be an adequate radical trap to stop alkene oxidation.

Nature of the Active Iron Porphyrin Oxidant. Various efforts were made to identify the nature of the iron porphyrin species responsible for alkene oxidation. Low-temperature generation and NMR spectroscopic observation of the oxidized $(TPP)FeF_2$ species by chemical oxidation was attempted without success. This involved addition of a solution of the iron(III) porphyrin π-cation radical species, $(p\text{-}OCH_3TPP)FeCl(ClO_4)$,[4d] to a dichloromethane solution of $(TPP)FeF_2^-$ containing excess $Bu_4NF{\cdot}3H_2O$ at −78

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(21) Ingelman-Sundberg, M.; Hagbjork, A.-L.; Ekstrom, G.; Terelius, Y. In *Cytochrome P-450, Biochemistry, Biophysics, and Environmental Implications*; Hietanen, E., Laitenen, M., Hanninen, O., Eds.; Elsevier: New York, 1982; pp 19–25.

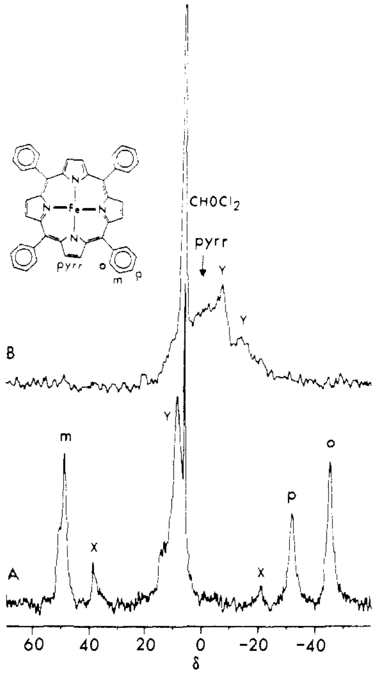

Figure 5. ^2H NMR spectra of fluoroiron(III) tetraphenylporphyrins oxidized by 0.9 mol equiv of MCPBA at -78 °C with CH_2Cl_2 as solvent and chemical shifts referenced to $(CD_3)_4Si$: (A) oxidized (TPP-*phenyl-d*$_{20}$)FeF, spectrum recorded at -46 °C; (B) oxidized (TPP-*pyrrole-d*$_8$)FeF, spectrum recorded at -65 °C. Peaks labeled "Y" are associated with porphyrin destruction products.

°C in an NMR tube. The iron(III) porphyrin radical species was reduced to the iron(III) porphyrin state, but resulting ^1H NMR signals could be assigned to the mono- and difluoroiron(III) porphyrin complexes. The $(TPP)FeF_2^-$ complex in dichloromethane at -78 °C was also treated with the oxidizing mixture composed of 1 equiv of iodine (in dichloromethane) and $AgNO_3$ (in acetonitrile).[22] The major $(TPP)FeF_2^-$ species was unaffected by the treatment.

Groves and co-workers have reported that addition of MCPBA to chloroiron(III) tetramesitylporphyrin, (TMP)FeCl, in 4/1 dichloromethane/methanol solutions at -78 °C produces an iron(IV) π-cation radical species capable of efficient olefin epoxidation.[8a] We have found that, in the absence of methanol, addition of 1 equiv of MCPBA to the chloroiron(III) tetraphenylporphyrin complex at -78 °C produced only the iron(III) porphyrin dimer, $[(TPP)Fe]_2O$. In contrast, addition of 0.9 mol equiv of the peracid to the fluoroiron(III) tetraphenylporphyrin complex (CH_2Cl_2 solvent, -78 °C, 2 mM iron porphyrin) produces a species that we have assigned an iron(IV) porphyrin π-cation radical electronic structure. The pyrrole ^1H NMR signal for this species is extremely broad, and use of deuterium-labeled material and ^2H NMR spectroscopy is required for reliable location of the signal (see Figure 5). The resulting broad signal (~500-Hz line width) is centered at -1 ppm (-65 °C). At -46 °C the phenyl ortho, meta, and para deuteron resonances are at -45.8, 48.1, and -32.5 ppm, respectively. These phenyl assignments were verified by comparison to the proton spectrum for the addition of MCPBA to (*p*-OMeTPP)FeF. In this instance the methoxy signal is located downfield at 49.4 ppm. Treatment of the analogous (TMP)FeF derivative with MCPBA yielded an NMR spectrum with no far upfield signal, thus confirming the *o*-phenyl proton assignment for the (TPP)Fe derivative. Signals at 99.3, 34.3, and 19.3 ppm at -50 °C are tentatively assigned to *m*-phenyl, *o*-methyl, and *p*-methyl residues of the (TMP)Fe-oxidized product. Addition of Bu_4NI as a reducing agent at low temperature served to generate the NMR spectrum of the $[(TPP)Fe]_2O$ species, thus indicating the reversibility of the process. The oxidized species was spontaneously reduced in the dichloromethane solution at temperatures higher than -23 °C. The predominant product from the autoreduction reaction was $[(TPP)Fe]_2O$, although partial destruction of the porphyrin was also apparent as noted below.

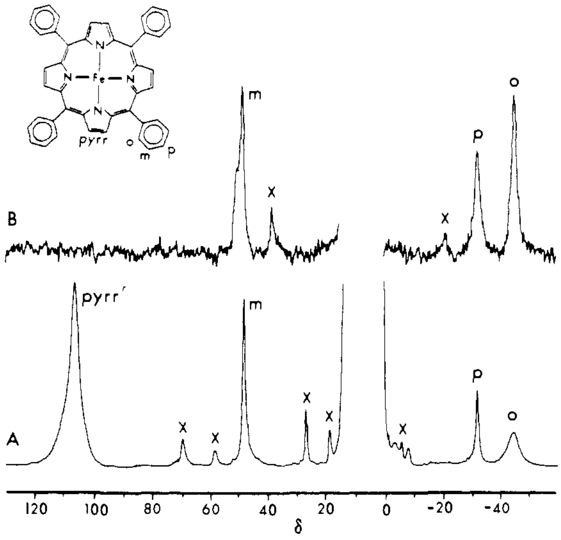

Figure 6. Parts: (A) ^1H NMR spectrum (360 MHz) of the products generated at -78 °C by reaction of $[(TPP)Fe]_2O(ClO_4)_2$ with excess $Bu_4NF{\cdot}3H_2O$, CD_2Cl_2 solution, and chemical shifts referenced to $(CH_3)_4Si$. (b) ^2H NMR spectrum (55 MHz) of (TPP-*phenyl-d*$_{20}$)FeF oxidized by 0.9 mol equiv of MCPBA in CH_2Cl_2 solution. Both spectra were recorded at -46 °C.

Use of excess MCPBA in attempts to drive the iron porphyrin oxidation reaction to completion resulted in production of new species with unresolved phenyl signals at 8 ppm (dichloromethane solvent, -62 °C) and pyrrole signals at -8 and -14 ppm. These peaks are also detected for solutions containing substoichiometric quantities of MCPBA and are labeled "Y" in Figure 5. Addition of Bu_4NI to the "overoxidized" species produced no change in the NMR spectrum. After the solution was warmed to ambient temperature, the typical iron porphyrin optical spectrum and Soret band were lost for the overoxidized species. Porphyrin-ring destruction is thus accompanied by use of excess MCPBA as the oxidant. A modified porphyrin product with the same NMR spectrum was also produced in significant quantities when the oxidized (TPP)FeF species was allowed to undergo autoreduction at temperatures above -23 °C.

An alternate pathway was devised for low-temperature generation of the new, reversibly oxidized iron porphyrin. Addition of a dichloromethane solution of the trihydrated Bu_4NF salt to the doubly oxidized iron(III) porphyrin radical dimer, $[(TPP)Fe]_2O(ClO_4)_2$, produces several NMR distinguishable species whose ratios are dependent on the number of equivalents of salt added. If a 4-fold molar excess (with respect to the iron concentration) of fluoride salt in dichloromethane is added at -78 °C, disproportionation of the oxo-bridged dimer occurs to yield (TPP)FeF (pyrrole signal at 105.9 ppm) and significant amounts of a species with phenyl proton resonances at -45.0 (ortho), 47.7 (meta), and -32.0 ppm (para) (spectra recorded at -46 °C). A stacked plot (see Figure 6) of the ^1H NMR spectrum of this mixture and the ^2D NMR spectrum of the species produced by the addition of MCPBA to phenyl-deuteriated (TPP)FeF suggests that these two reactions produce one major, common oxidized species. (The ^1H NMR spectrum in Figure 6 does not reveal the presumably very broad pyrrole signal that is lost due to overlap with the butylammonium signals). Additional signals labeled as "X" in the far downfield region of Figure 6A must represent those for other iron porphyrin radical species, such as $(TPP)Fe(F)(ClO_4)$.

Electron spin resonance data also support an iron(IV) π-cation radical $S = {}^3/_2$ designation for the reactive intermediate. At liquid-helium temperature *g* values of 4.32, 3.77, and 3.27 have been reported for the putative oxoiron(IV) π-cation radical species

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[22] Kadish, K. M.; Rhodes, R. K.; Bottomley, L. A.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3195-3200.

generated by iodosylbenzene oxidation of the iron(III) porphyrin.[23] Addition of stoichiometric amounts of MCPBA to (TPP)FeF at 195 K (dichloromethane solvent) produces a species with EPR signals at $g = 4.2$, 3.9, and 3.5 at 5 K.

Competency of the oxidized species to effect alkene functionalization was verified. The $Bu_4NF{\cdot}3H_2O$ salt was added to the doubly oxidized dimer, $[(TPP)Fe]_2O(ClO_4)_2$, contained in a 10% cyclohexene/dichloromethane solution at −78 °C. The result was a highly efficient epoxidation of the cyclohexene with only traces of enol and enone produced. An overall product yield of greater than 90% was obtained on the basis of the oxidizing equivalents of the oxidized dimer.

Discussion

The first oxidation wave for most five-coordinate high-spin iron(III) tetraphenylporphyrin adducts is 1.10 ± 0.02 V.[4a,17] It is well-established that this potential is associated with porphyrin-centered oxidation and π-cation radical formation.[4] The lower oxidation potential of 0.68 V for $(TPP)FeF_2^-$ and the high reactivity of the oxidized product suggest a different electronic structure. Metal-centered oxidation of $(TPP)FeF_2^-$ to give a difluoroiron(IV) porphyrin as the *immediate* electrochemical product is a viable possibility. In this regard, Bruice and coworkers, Groves and co-workers, and Kadish and co-workers have provided evidence for metal-centered electrochemical oxiation of methoxide- and hydroxide-ligated iron(III) porphyrins.[5] Groves and co-workers have also shown that coordination of two methoxide ligands to iron(III) porphyrin π-cation radicals is sufficient to induce rearrangement to the iron(IV) state.[7] Although a case can be made for the direct electrochemical production of a $(TPP)Fe^{IV}F_2$ species, its spectroscopic detection even at low temperatures has been hindered by rapid conversion to another oxidized species or reduction to the parent iron(III) porphyrin.

The anodic current and the i_{pa}/i_{pc} ratio increased with increasing concentration of the fluoride salt present in solution. This suggests that the irreversibility may be partly due to an ECE type mechanism by which the reactive oxoiron species is reduced to the difluoroiron(III) complex with initiation of a catalytic cycle or is reduced to a new product that is also electroactive at +0.68 V. The overlap of two anodic waves is evident at scan rates lower than 10 mV/s, which is in agreement with the latter mechanism. The second wave is likely due to the oxidation of a product formed following the disproportionation reaction. The most probable product is $[(TPP)Fe]_2O$, which is oxidized at approximately 0.8 V. At such very low scan rates the addition of 10% cyclohexene or lowering of the temperature results in an increase in the reversible nature of the CV profiles and sharpening of the anodic wave through disappearance of the second-oxidation process. The above-mentioned changes in the CV profiles with temperature are similar to the oxidation of (TMP)FeOH reported recently by Kadish et al.[5e] The CV profiles at scan rates higher than 20 mV/s do not show the above-mentioned features due to the smaller time scale.

Absence of catalytic waves for cyclic voltammograms in which cyclohexene is combined with the $(TPP)FeF_2^-$ "electrocatalyst" serves to demonstrate that the immediate oxidation product is not responsible for alkene oxidation. Furthermore, conversion of alkenes to epoxides and alcohols represents a two-electron oxidation process, even though electrolyses were conducted only at the first oxidation wave. The short lifetime of the oxidized difluoroiron(III) porphyrin and the net two-electron alkene oxidations can best be explained by a sequence of hydrolytic and disporportionation reactions in which water from the hydrated $Bu_4NF{\cdot}3H_2O$ salt is involved. Water was shown to facilitate the EC process for experiments in which dichloromethane was saturated with water. As expected, the EC process is quite temperature-dependent.

The spectroscopic and reactivity properties described below are consistent with an ultimate oxidant that bears a porphyrin π-cation radical, that has iron in the 4+ oxidation state, and that has a requirement for fluoride- and oxygen-based ligands. The species is tentatively formulated as (TPP)Fe(F)(O) and accordingly must be oxidized two steps above the parent iron(III) porphyrin. Precedent exists for a disproportionation reaction in which $(TPP)Fe^{IV}F_2$ might serve as the oxidant for a hydrolyzed fluoroiron(IV) porphyrin to generate the fluorooxoiron(IV) porphyrin π-cation radical species. In particular, two research groups have recently shown that the iron(III) porphyrin π-cation radical species $(TMP)Fe(ClO_4)_2$ is suitable for conversion of an oxoiron(IV) porphyrin to the oxoiron(IV) porphyrin π-cation radical state.[24] A photodisproportionation reaction that yields a putative iron(IV) porphyrin has also been elucidated for the iron(III) dimer $[(TPP)Fe]_2O$.[25] Schemes that summarize the likely electrochemical and chemical pathways involving fluoroiron porphyrin species described here are shown in Figure 7.

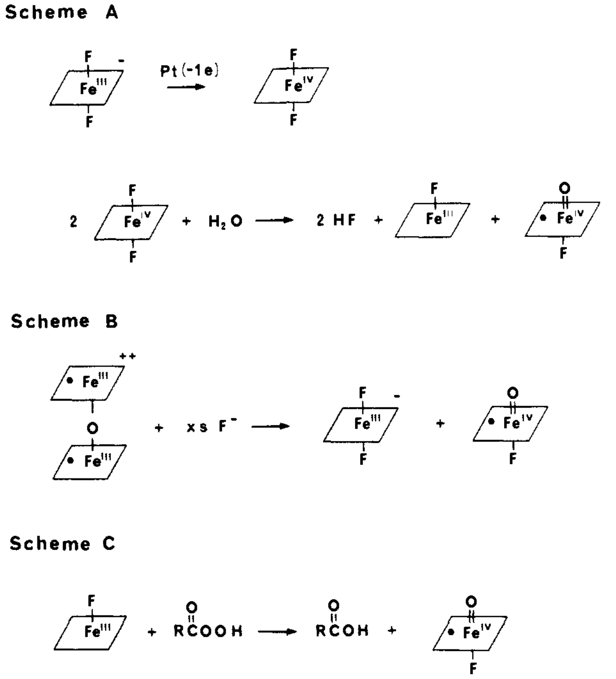

Figure 7. Proposed schemes for the generation of high-valent iron porphyrin species involved in hydrocarbon oxidation: (A) one-electron electrochemical oxidation followed by intervention of water and disproportionation; (b) fluoride ion cleavage of the doubly oxidized μ-oxo dimer species; (C) direct oxo transfer from MCPBA ($R = C_6H_4Cl$).

Low-temperature NMR measurements provide the most detailed information concerning the electronic structure of the high-valent iron porphyrin product. Observation of alternating far downfield and far upfield phenyl proton (deuteron) signals is diagnostic of a porphyrin π-cation radical species.[20] The broad pyrrole deuteron signal at −1 ppm does not match known values for iron(II) or iron(III) tetraarylporphyrins,[19,20] and the only precedent for such a signal is found in compounds for which an iron(IV) oxidation state has been assigned. Reported pyrrole resonances for iron(IV) prophyrin and iron(IV) porphyrin π-cation radical species range from +8.5 to −37.5 ppm at dry-ice temperature.[5b,6a,c,7,8,24] Specifically, the oxoiron(IV) tetramesitylporphyrin π-cation radical species in a toluene/methanol mixture at −70 °C exhibits a pyrrole proton signal in the −17 to −27 ppm region.[5b,8a] Molecular orbital calculations indicate that ferryl radical and nonradical porphyrin species have the preponderance of unpaired electron spin density localized on the oxygen atom.[26] It would thus seem likely that axial ligation could greatly affect

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[23] Groves, J. T.; Quinn, R. Presented at the 189th National Meeting of the American Chemical Society, Miami Beach, FL, 1985; INOR 11.

[24] (a) Balch, A. L.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2983–2985. (b) Groves, J. T.; McMurry, T. J. *Rev. Port. Quim.* **1985**, *27*, 102–103.

[25] (a) Peterson, M. W.; Richman, R. M. *Inorg. Chem.* **1985**, *24*, 722–725. (b) Peterson, M. W.; Rivers, D. S.; Richman, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 2907–2915.

[26] Hanson, L. K.; Chang, C. K.; Davis, M. S.; Fajer, J. *J. Am. Chem. Soc.* **1981**, *103*, 663–670.

the amount of electron density localized on the oxygen and thus on the β-pyrrole position. This may rationalize the difference seen in the β-pyrrole NMR resonances for the presumed methanol or methoxide and fluoride ligation to the oxoiron(IV) porphyrin π-cation radical species. Electron spin resonance spectra at liquid-helium temperature are quite similar for the two types of complexes, and the spectra are most representative of a $S = {}^3/_2$ state. This formulation would thus require ferromagnetic coupling between the $S = {}^1/_2$ porphyrin radical and a low-spin $S = 1$ iron(IV) center.[8b]

Involvement of the fluoride ion as a ligand in the high oxidation state species is suggested by the unique role of this ion in either the MCPBA or the oxidized iron porphyrin dimer preparative routes. A methanol requirement for MCPBA oxidation of other iron(III) porphyrin complexes to the iron(IV) porphyrin π-cation radical state likely reflects the importance of a basic ligand (i.e., methoxide ion) in combination with the putative oxo ligand. The presence of an oxo ligand in the chemically and electrochemically generated high-valent fluoroiron porphyrin complexes is inferred by analogy to the previously observed stereochemical preference for *cis*- but not *trans*-stilbene epoxidation.[27] Orthogonal orientation of the phenyl groups of (TPP)Fe provides a restricted heme environment such that an iron–oxene–substrate interaction is favorable only for the *cis*-stilbene isomer. Presumably, a free radical reaction in which substrates need not interact with the iron center would show little discrimination toward the stilbenes.

Free-radical pathways cannot be excluded, however, and appearance of sizable quantities of the allylic alcohol and ketone oxidation products of cyclohexene could be taken as evidence for free-radical involvement. The radical-trap experiments neither refute nor implicate free-radical pathways, as the reactivity of the radical trap and the high-valent iron porphyrin intermediate is unknown. Differing ratios of cyclohexene oxidation products for low-temperature oxidation by the high-valent fluoroiron porphyrin complex (from oxidized μ-oxo dimer and fluoride ion) and ambient-temperature electrochemical oxidation are noteworthy. Cyclohexene oxide is produced almost exclusively at low temperature, whereas a nearly equimolar mixture of cyclohexene oxide, alcohol, and ketone appear in the electrolysis mixture. This observation might be taken as evidence for multiple-reaction pathways with different activation energies. Accumulation of acid in the electrochemical cell in conjunction with oxo-group transfer from water is problematic, in that the epoxide could potentially be opened to the allylic alcohol. However, comparison of the reaction mixture after 5 min of electrolysis with that obtained after 1 h revealed no difference in the relative concentrations of the three oxidation products.

Metalloporphyrins have been utilized as mediators with various chemical oxidants to effect hydrocarbon oxidation. An excellent review article is available on the subject.[28] With regard to the composition of products that result from iron-porphyrin-catalyzed olefin oxidation, the relative yields of epoxide are generally higher for the chemical systems than for the electrocatalytic system described here. For example, the ratio of cyclohexene oxide to allylic alcohol product is approximately 4/1 for either iodosylbenzene[27a] or 4-cyano-*N*,*N*-dimethylaniline *N*-oxide[29] oxidation of cyclohexene mediated by (TPP)FeCl. No significant quantities of the enone are produced by either of these chemical systems. In contrast, nearly equivalent quantities of the epoxide, allylic alcohol, and enone result from ambient-temperature electrocatalysis by $(TPP)FeF_2^-$. Product profiles for the electrochemical system are intermediate between those mediated by iron porphyrins and chromium porphyrins for iodosylbenzene oxidation of cyclohexene in that the (TPP)CrCl catalyst gives predominantly alcohol and enone with little epoxide product.[30]

Two other metalloporphyrin-mediated electrooxidation systems have been described for olefin oxidation. The chromium porphyrin system is stoichiometric through oxidative activation of a chromium(IV) reactant.[31] Norbornene is oxidized exclusively to the epoxide by the putative $(TPP)Cr(O)^+$ species, but a direct reaction with the parent chromium(IV) species and cyclohexene precluded further electrochemical investigation of this substrate. Sterically hindered iron porphyrins are also shown to function as electrocatalysts in the presence of hydroxide ion.[5b] Although direct comparison with cyclohexene as a substrate is not possible, a disproportionation pathway is also proposed to explain the two-electron oxidation of olefins to epoxides at the first oxidation wave of the iron porphyrin catalyst.[5b]

Conclusions

Efficient electrochemical oxidation of alkenes and tertiary alkane carbon sites is promoted by difluoroiron(III) porphyrin complexes contained in aprotic organic media. Porphyrin destruction is not a problem in the presence of excess substrate. Water of hydration introduced along with the excess fluoride salt presumably serves as the source of oxygen through a hydrolytic disproportionation reaction of the oxidized difluoroiron porphyrin species. Low-temperature experiments have permitted spectroscopic identification of a chemically oxidized iron porphyrin species capable of efficient olefin epoxidation. Generation of the oxidized iron porphyrin is dependent on the presence of fluoride ion, and hence the proposed structure of the active oxidant includes axial fluoro and oxo ligands coordinated to an iron(IV) porphyrin π-cation radical center. This structure is analogous to that of peroxidase compound I and to the proposed active intermediate of cytochrome P-450.

Acknowledgment. This project was supported by National Science Foundation Grants CHE 83-17451 and CHE 87-05703.

Registry No. MCPBA, 937-14-4; (TPP)FeF, 55428-47-2; $(TPP)FeF_2^-$, 76402-68-1; ((TPP)-*phenyl*-d_{20})FeF, 115795-93-2; ((TPP)-*pyrrole*-d_8)-FeF, 115795-94-3; (*p*-OMeTPP)FeF_2^-, 86646-34-6; $(TPP)FeF_2$, 115825-94-0; H_2O, 7732-18-5; Pt, 7440-06-4; $Bu_4NF{\cdot}3H_2O$, 22206-57-1; Bu_4NClO_4, 1923-70-2; Pr_4NClO_4, 15780-02-6; Bu_4NI, 311-28-4; $[(TPP)Fe]_2O(ClO_4)_2$, 72319-58-5; cyclohexene, 110-83-8; cyclohexenone, 25512-62-3; 2-cyclohexen-1-ol, 822-67-3; cyclohexene oxide, 286-20-4; *cis*-stilbene, 645-49-8; *cis*-stilbene epoxide, 1689-71-0; cyclohexane, 110-82-7; 2,2,4-trimethylpentane, 540-84-1; 2,4,4-trimethylpentan-2-ol, 690-37-9; diphenylpicrylhydrazine, 1707-75-1; 1,8-bis(dimethylamino)naphthalene, 20734-58-1.

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