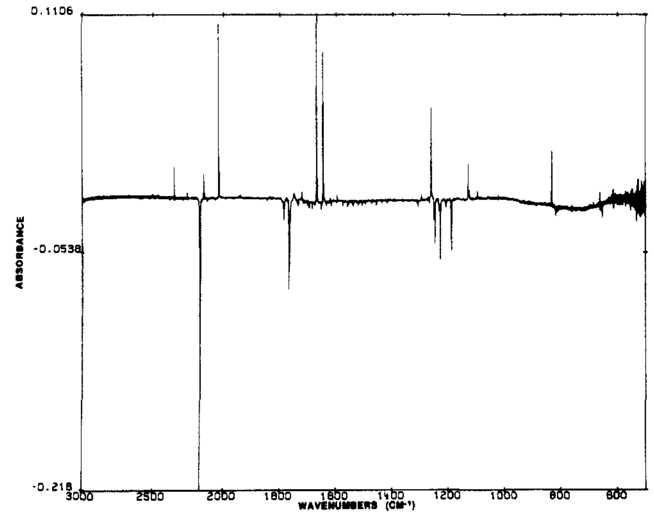


Figure 1. IR difference spectrum from the brief monochromatic photolysis (λ = 240 nm) of difluoropropadienone (DFP) in a $^{15}N_2$ matrix at 11 K. Bottom portion is DFP that has been lost and top is difluorodiazoethene that has been formed during the reaction.

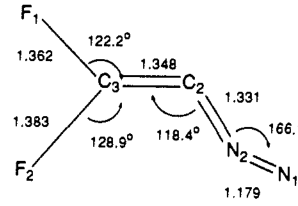
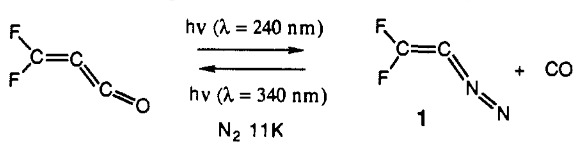


Figure 2. MP2/4-31G optimized structure for difluorodiazoethene. Bond lengths are in angstroms.

This intermediate quickly reached a photochemical steady state concentration of approximately 2% that of DFP. Similar monochromatic irradiation of isotopically labeled DFP containing ^{13}C in the carbonyl position[11] produced the same IR spectrum, implying the absence of CO in the intermediate. An analogous matrix experiment employing the normal isotopomer and $^{15}N_2$ as the matrix material caused a shift for all the IR bands, implying that nitrogen is present in the intermediate. A difference spectrum for the $^{15}N_2$/normal isotopomer experiment is shown in Figure 1. The new intermediate quantitatively reverts to DFP upon irradiation at longer wavelengths (λ = 340 ± 10 nm). On the basis of this fact and the IR data of the isotopic species, the intermediate is assigned as difluorodiazoethene (**1**).



As a further aid in the assignment of this structure, we have carried out ab initio calculations[14] on difluorodiazoethene.[15] The MP2/4-31G optimized structure is shown in Figure 2.[16] A frequency calculation at this level of theory predicted (unscaled) IR bands (with relative intensities) at: 2071 (0.56), 1647 (1.00), 1232 (0.17), 1101 (0.11), 812 (0.05), 614 (0.03), 603 (0.00), 558 (0.00), 476 (0.01), 436 (0.00), 170 (0.00), and 160 cm^{-1} (0.00). The agreement with Table I is very reasonable.[17] At the MP3/6-31G* level, the reaction of DFP plus nitrogen leading to **1** plus carbon monoxide is calculated to be endothermic by 50 kcal/mol. Fragmentation of **1** to DFV and nitrogen is calculated to be endothermic by 25 kcal/mol.

While diazoethenes have been postulated as reactive intermediates in solution,[18] they had not been detected spectroscopically. In contrast to other diazoethenes, **1** owes its existence and spectroscopic detection to the fact that DFV is kinetically much more stable to rearrangement than vinylidene.[19] This allows DFV to be generated reversibly from DFP under photochemical conditions without rearrangement to difluoroacetylene. In the absence of a suitable trapping agent (nitrogen), the thermal back-reaction to reform DFP is very facile under the matrix conditions and direct detection of DFV is not possible. Gas-phase flash photolytic conditions will eliminate this back-reaction, and direct spectroscopic observation of difluorovinylidene will be possible. Such experiments are underway and will be reported in due course.

Acknowledgment. We are grateful to the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8822674) for support of this work.

Supplementary Material Available: Ab initio HF/6-31G* optimized geometries and MP2 and MP3 single point energies for DFP, DFV, and **1** as well as general experimental procedures and spectroscopic properties of the DFV adducts with cyclopentene (7 pages). Ordering information is given on any current masthead page.

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[14] The calculations employed Gaussian 88: M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Ragavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA.

[15] (a) A semiempirical study of difluorodiazoethene has been reported. See: Lahti, P. *Chem. Phys. Lett.* **1987**, *133*, 139. (b) A similar ab initio study on the parent diazoethene has recently appeared. See: Murcko, M. A.; Pollack, S. K.; Lahti, P. M. *J. Am. Chem. Soc.* **1988**, *110*, 364.

[16] Very similar structures were also obtained at the HF/6-31G* and MP2/6-31G* levels, but a frequency calculation at the latter level was prohibitively expensive.

[17] The IR bands at 2100 and 1650 cm^{-1} are assumed to be doubled due to matrix site defects. All the bands assigned to difluorodiazoethene grew in or disappeared at the same rate during its formation or destruction.

[18] Newman, M. S.; Okorodudu, A. O. M. *J. Am. Chem. Soc.* **1968**, *90*, 4189; *J. Org. Chem.* **1969**, *34*, 1220. (b) Newman, M. S.; Patrick, T. B. *J. Am. Chem. Soc.* **1969**, *91*, 6461. (c) Newman, M. S.; Liang, W. C. *J. Org. Chem.* **1973**, *38*, 2438. (d) Gilbert, J. C.; Weerasooriya, U.; Giamalva, D. *Tetrahedron Lett.* **1979**, 4619. (e) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1979**, *44*, 4997. (f) Gilbert, J. C.; Weerasooriya, U.; Weichman, B.; Ho, L. *Tetrahedron Lett.* **1980**, 5003. (g) Lahti, P. M.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7011. (h) Fox, D. P.; Bjork, J. A.; Stang, P. J. *J. Org. Chem.* **1983**, *48*, 3994. (i) Bruckmann, R.; Maas, G. *Chem. Ber.* **1987**, *120*, 635.

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Electrocatalytic Hydroxylation of Alkanes and Identification of a Fluoroiron(V) Porphyrin Intermediate

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High-valent iron porphyrin models for the active intermediate in the cytochrome P-450 cycle have been generated and used as catalysts for the selective epoxidation of alkenes and hydroxylation of alkanes.[1] In this regard, metallotetraarylporphyrins with electronegative substituents at the *o*-aryl position have been investigated due to their remarkable stability toward oxidative degradation and resistance to formation of dinuclear μ-oxo iron porphyrin complexes.[2,3] The horseradish peroxidase compound

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[1] (a) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884-2886. (b) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786-5791. (c) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 507-508. (d) Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, 578-594.

[2] Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279-280.

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I analogue of the cytochrome P-450 cycle is generally believed to be the doubly oxidized (oxo)iron(IV) porphyrin π-cation radical species. The isoelectronic (oxo)iron(V) porphyrin structure has also been proposed,[1] but no model complexes have been identified with both oxidation equivalents at the metal center.

The electrochemical oxidation of $(TPP)FeF_2^-$ results in the generation of a (fluoro)(oxo)iron(IV) porphyrin π-cation radical intermediate species that was shown to cause efficient epoxidation of alkenes.[4,5] The difluoroiron(III) porphyrin complex is generated by addition of excess hydrated tetrabutylammonium fluoride salt ($TBAF{\cdot}3H_2O$) to (TPP)Fe(III)F. The water from the hydrated fluoride salt provides the oxygen source.[5] The inability of the active intermediate to oxidize alkanes was attributed to a thermodynamic limitation due to a relatively low oxidation potential of approximately 0.7 V. This work describes the electrocatalytic hydroxylation of cyclohexane with the difluoroiron(III) 2,6-difluorotetraphenylporphyrin anionic complex, $[(F8\text{-}TPP)FeF_2^-]$. Magnetic resonance and optical spectroscopic measurements have been used to elucidate the electronic structure of the product formed following oxidation of $(F8\text{-}TPP)FeF_2^-$ by *m*-chloroperbenzoic acid (MCPBA) in the presence of excess fluoride ion. Measurements are consistent with formation of an iron(V) porphyrin complex, which presumably is also an intermediate in the electrocatalytic process. The high-valent iron porphyrin species is sufficiently stable to be detected even at ambient temperature. This is the first evidence for an iron(V) porphyrin structure.

A drastic change in the peak potential for the first oxidation wave of the difluoroiron(III) tetraarylporphyrin anion is observed upon *o*-fluoroaryl substitution ($E_{p,a}$ = 0.70, 1.15, and 1.40 V vs SCE for the unsubstituted, 2,6-difluorophenyl-substituted, and pentafluorophenyl-substituted complexes, respectively). Because the oxidation potential of $(F20\text{-}TPP)Fe(III)F_2^-$ is in the region of the anodic potential limit of dichloromethane solvent, the electrocatalytic studies were limited to the $(F8\text{-}TPP)Fe(III)F_2^-$ complex. A dichloromethane solution (5 mL) that contained 10% cyclohexane, (F8-TPP)Fe(III)F (2 mM), $Bu_4NF{\cdot}3H_2O$ (0.02 M), and Pr_4NClO_4 (0.10 M) was electrolyzed at potentials slightly positive of the observed oxidation wave with a 1 cm diameter platinum basket working electrode (N_2 agitation). Reference and counter electrodes were separated from the bulk solution by very fine glass frits. After 1 h, the current dropped to approximately 10% of the initial value as acid production converted excess fluoride ion to bifluoride ion. Spectroscopic measurements at this point revealed that the principal porphyrin species was (F8-TPP)Fe(III)F. 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. Cyclohexanol was identified as the principal oxidation product, and the turnover number (moles of cyclohexanol/initial moles of (F8-TPP)FeF) was approximately 10. This yield could be increased by repeated electrolysis after addition of more fluoride salt. Electrocatalytic studies using octane as a substrate produced lower yields of 2-octanol, 3-octanol, and 4-octanol (1:1:1 ratios), but hydroxylation at the primary carbon position was not observed.

Efforts were made to identify possible high-valent iron porphyrin intermediates through chemical oxidation. The halogenated tetraaryl iron porphyrins are known to serve as effective catalysts for peracid oxidation of alkanes.[2,3] Figure 1 shows the pyrrole deuteron NMR signal of $(pyrr\text{-}d8\text{-}F8\text{-}TPP)Fe(III)F_2^-$ along with the signal for the MCPBA oxidation product in dichloromethane at 210 K. The pyrrole deuteron signal at +1.3 ppm is in the region associated with partial occupation of d_{xy} and/or d_{xz} orbitals.[5] This peak is also detected at 298 K, but is rapidly (minutes) converted to the $(F8\text{-}TPP)Fe(III)F_2^-$ complex along with partial destruction of the porphyrin. The pyrrole deuteron signal for the oxidized species shows Curie law behavior from 220 to 270 K (chemical shift vs $1/T$ (K^{-1}) with a *y* intercept of 7.3 ppm). Phenyl proton NMR signals are located at 9.0 and 15.0 ppm, unlike the case for iron porphyrin cation radical species that show much larger odd-alternate shifts.[5]

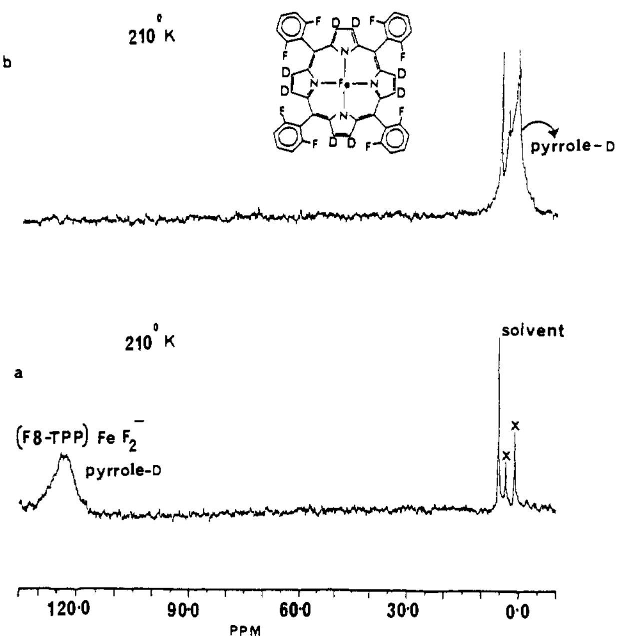

Figure 1. ^2H NMR spectrum (55 MHz) of $(pyrr\text{-}d8\text{-}F8\text{-}TPP)Fe(III)F_2^-$ and the product formed following MCPBA oxidation; dichloromethane solvent, 210 K, TMS reference: (a) (pyrr-d8-F8-TPP)Fe(III)F (4.5 mM), $TBAF{\cdot}3H_2O$ (0.1 M); (b) after addition of MCPBA (50 mM). Peaks labeled x are due to $TBAF{\cdot}3H_2O$ salt.

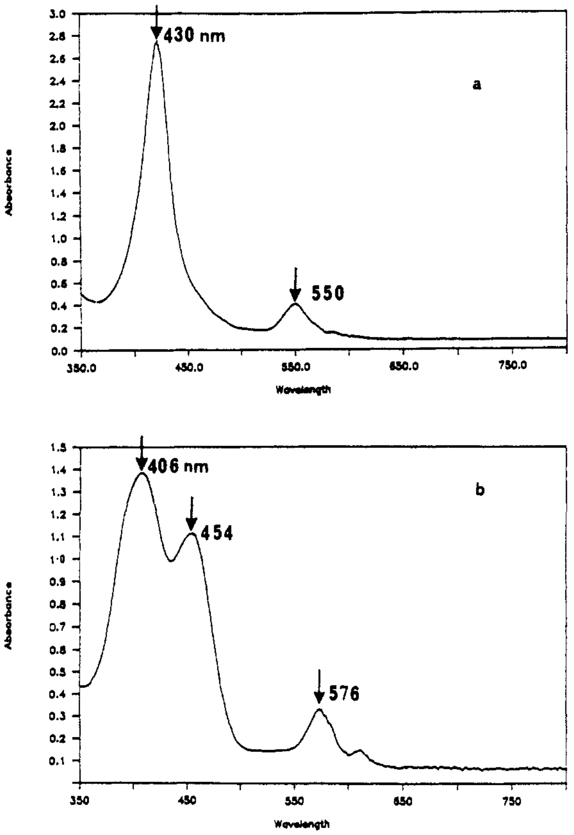

Figure 2. UV-visible spectrum of the product formed following MCPBA oxidation of $(F8\text{-}TPP)Fe(III)F_2^-$; dichloromethane solvent, 298 K: (a) (F8-TPP)Fe(III)F (2.5×10^{-5} M), $TBAF{\cdot}3H_2O$ (0.05 M), MCPBA (4.0×10^{-3} M); (b) solution of part a after 15 min at 298 K.

The MCPBA oxidation product is a distinct red color with optical spectral bands at 430 nm (Soret) and 550 nm at ambient temperature (Figure 2a), similar to the spectra reported for (oxo)iron(IV) porphyrin species,[6] but clearly distinct from those

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for porphyrin cation radicals.[7] The new spectral features disappear after 10-15 min with the appearance of bands due to (F8-TPP)Fe(III)F_2^- (a split Soret band is observed at 406 and 454 nm with an additional band at 576 nm, Figure 2b).

The EPR spectrum for the MCPBA-oxidized product shows the presence of three distinct signals at $g = 4.38$, 3.11, and 2.70 at 80 K (a broad $g = 2$ signal due to destruction product is present if a large excess of MCPBA is added to bleach the porphyrin). The solution magnetic moment (210 K) is $4.1 \pm 0.2\ \mu_B$. Detection of EPR signals characteristic of a $S = {}^3/_2$ species at moderate temperature in concert with the magnetic moment is consistent with generation of an iron(V) porphyrin species, since an iron(IV) porphyrin complex ($S = 1$) is expected to be EPR silent. Other possible structures such as the (oxo)iron(IV) porphyrin π-cation radical species would be expected to show a blue shift in the Soret band,[7] unlike the optical spectra observed here.

These spectroscopic results are observed only in the presence of a large excess of fluoride ion. Hence coordination of a fluoro ligand or ligands is suggested for the iron(V) complex. Double oxidation of the metal center is favored in this case by virtue of a relatively electron deficient porphyrin framework. On the basis of the observed results, a structure with coordinated fluoro ligands or a combination of oxo and fluoro ligands is suggested for the iron(V) porphyrin species.

Acknowledgment. This project was supported by National Science Foundation Grant CHE 87-05703. NMR spectroscopy was performed in the University of Iowa High Field NMR Facility.

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Chromophore Aggregation and Concomitant Wavelength-Dependent Photochemistry of a Main-Chain Liquid Crystalline Poly(aryl cinnamate)

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The unique combination of order and mobility has made liquid crystalline (LC) media attractive for photochemical studies, and there are now many examples[1] of such uses of low molar mass LC materials. We have recently reported the first observations[2] of the effects of LC behavior on main-chain polymer photochemistry using a class of novel main-chain thermotropic LC polymers (e.g., **1**, Chart I), in which fairly rigid aryl cinnamate mesogenic groups are connected by flexible spacer groups. In our continuing efforts to delineate the influence of order and mobility on these photoreactions, we have obtained evidence that aggregation of the chromophores in parallel or near-parallel stacks leads to a wavelength dependence of the polymer photochemistry. This effect is most dramatic in the glassy nematic phase of the polymer and is the first such observation in the photochemistry of either a low molar mass or polymeric LC material.

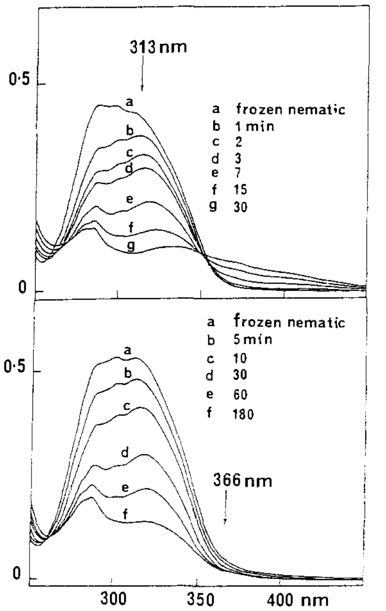

Figure 1. UV-vis spectral changes upon 313- and 366-nm irradiation of a glassy nematic film of polymer **1**. The remaining absorption at ca. 280 nm is attributed to cyclobutane photoproducts. The long-wavelength absorption stretching into the visible region is attributed to photo-Fries product.[2,7]

Polymer **1** is nonbirefringent[3] when cast from chloroform. The highest molecular weight preparations become nematic above 70 °C and finally isotropic above 120 °C. Clearing temperatures are molecular-weight dependent.[4] On cooling to room temperature, the nematic phase is retained in a glassy state in which LC order is frozen in. Drastic UV spectral changes are observed in the nematic state, and the overall broadening and increase in absorption to the blue and to the red of the original band that accompanies the drop in the optical density is attributed to the formation of aggregates by a significant fraction of the aryl cinnamate chromophores.[2] Additional evidence for this hypothesis comes from duplication of these spectral changes using dispersions of the small-molecule model copound, **2**, in poly(methyl methacrylate), PMMA. In dilute dispersions (<10% of **2**), the unaggregated monomer is observed at $\lambda_{max} = 317$ nm. With sufficiently high fractions of **2** in PMMA, a new blue-shifted band ($\lambda_{max} = 280$ nm) can be seen in the UV, with weaker absorption stretching into the visible. Such behavior is characteristic of near-parallel stacking of chromophores.[5] The magnitude of the hypochromic effect in the polymer is dependent on the molecular weight.[6] These effects will be discussed in more detail in a subsequent full paper.

Two major photochemical reactions occur[2] upon irradiation of films of **1** at 313 nm. These are cyclobutane formation, shown by UV absorption changes and solid-state ^{13}C NMR, and photo-Fries rearrangement, shown by comparison of a new UV-vis absorption band with the UV-vis absorption of the photo-Fries product, **3**, obtained from irradiation[7] of **2**. The UV-irradiated films become insoluble, indicating a significant amount of cross-linking, most probably via interchain cinnamate dimerization. A small fraction of other reactions leading to saturation of the cinnamate double bond cannot be completely excluded.[8] The

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(3) Freshly cast films of **1** show a slight opacity suggesting some local ordering of the chains. Moreover, samples with no thermal history exhibit a broad endothermic transition above 50 °C in DSC scans, that is absent in the (reproducible) second and subsequent heating cycles. This transition is also consistent with some local order present in the material before it is heated into the nematic or isotropic phases.

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