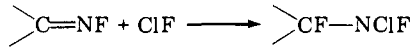
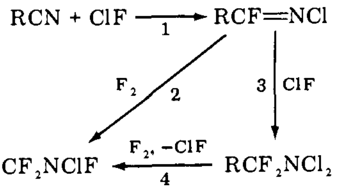
Five examples of *N*-chloro-*N*-fluorofluoroalkylamines are known, CF_3NClF,[1,2] $ClCF_2NClF$,[2] $(CF_3)_2CFNClF$,[2] $Cl_2CFNClF$,[2] and CH_3CF_2NClF.[3] These compounds were prepared by reactions of the corresponding *N*-fluoroimines with ClF, except for the last example which was obtained from CH_3CN and ClF_5.[2,3] The *N*-fluoroimines are very difficult to



$$CH_3CN + ClF_5 \longrightarrow CH_3CF_2NClF$$

prepare except for $(CF_3)_2C{=}NF$, which is available in good yield via the fluorination of $(CF_3)_2C{=}NH$ in the presence of CsF.[4] The reaction with ClF_5 has obvious potential dangers. As a result of these synthetic limitations, little is known about the chemistry of *N*-chloro-*N*-fluoroalkylamines.

By reaction of a mixture of ClF and F_2 with some halogenated nitriles, high yields of *N*-chloro-*N*-fluoroamines can be obtained. With RCN, the following reaction sequence is now reasonably well established (R = Cl, CF_3, C_2F_5). The reactions



are carried out by condensing 3 mmol of each reactant into a 75-mL stainless steel reactor at −195 °C. The mixture is then warmed to 22 °C over 1 h and allowed to stand at 22 °C for 4, 40, or 63 h for RCN (R = Cl, CF_3, and C_2F_5, respectively). The yields are >90% in each case. Under these conditions, ClF does not react with F_2 forming ClF_3, and F_2 does not react with RCN. Reactions 1 and 3 are known[5] and 2 and 4 were confirmed independently by reaction of $RCF{=}NCl$ and RCF_2NCl_2 with F_2. The mixture of F_2–ClF is more effective than ClF (reactions 1 and 3) followed by F_2 (4). Yields are considerably lower by this route. $ClCF_2NClF$ was identified by comparison of ^{19}F NMR and IR spectra and molecular weight with literature values.[2] The new compounds, CF_3CF_2NClF and $CF_3CF_2CF_2NClF$, exhibit the expected NMR and IR spectra and molecular weight. Attempts to extend the reaction to nonhalogenated nitriles using CH_3CN resulted in explosions at −195 °C.

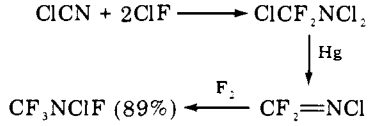
A special interest in synthesizing RCF_2NClF was to prepare $CF_2{=}NF$, the simplest fluorinated imine. This novel molecule has been nearly unavailable for chemical studies.[2,6,7a] The synthesis of $CF_2{=}NF$ can be carried out by reaction of $ClCF_2NClF$ with mercury.[2] On a 3-mmol scale CF_3Cl is a major byproduct, and it is very difficult to separate from $CF_2{=}NF$, even by efficient GLC. By carrying out the reaction of $ClCF_2NClF$ with Hg in the CF_3CO_2H (TFA) solvent, the CF_3Cl byproduct is eliminated forming $CF_2{=}NF$ in 90% yield.

Extension of this reaction to CF_3NClF, C_2F_5NClF, and *n*-C_3F_7NClF afforded surprisingly different results. The reactions give high yields of R_fNHF, 90–95%. The previously

$$R_fNClF + \xrightarrow[22\ ^\circ C]{TFA/Hg} R_fNHF$$

$$R_f = CF_3,\ C_2F_5,\ \text{or}\ n\text{-}C_3F_7$$

reported amine, CF_3NHF,[7] was identified by comparison of IR and NMR spectra and molecular weight with literature values. The new compounds, C_2F_5NHF and *n*-C_3F_7NHF, exhibit the expected IR and NMR spectra and molecular weight. They are the only other reported examples of a secondary fluoroperfluoroalkylamine. The earlier syntheses of CF_3NHF are difficult. Now by the sequence shown, combined with the above reaction, the compound is easily prepared.



Addition of F_2 to $CF_2{=}NCl$[5a] was not previously known and previous preparations of CF_3NClF are difficult.[1,2]

Caution! Some of the reactions involving mixture of ClF and F_2 are potentially explosive. R_fNClF and R_fNHF may also be explosive, although no explosive decompositions have been observed in this work.

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Oxidation of μ-Oxo-Bridged Iron Porphyrin Dimers

Sir:

The existence of iron(IV) and its role as an intermediate in hemoproteins such as catalases, perioxidases, and cytochrome P-450 are topics of considerable current interest. Modern spectroscopic methods verify metal oxidation in peroxidases,[1] but adequate models for high oxidation state hemoproteins have yet to be reported. A major question concerning oxidation of isolated iron porphyrins is whether electron abstraction is formally from a metal or ligand based molecular orbital. Preparation of well-defined oxidized species is clearly prerequisite to answering this and other questions relevant to hemoprotein oxidation. Felton et al. reported preliminary electrochemical oxidation of monomeric and dimeric iron porphyrin species.[2] One-electron oxidation of μ-oxo-bis-5,10,15,20-tetraphenylporphyrinatoiron(III), $[FeTPP]_2O$, yielded a presumed mixed oxidation state dimer, $[Fe^{III}\text{-}O\text{-}Fe^{IV}]^+$. We have extended this work to isolation of the doubly oxidized dimeric species and further characterization of solution properties. Preliminary results reveal the doubly oxidized dimer as a desirable oxidizing agent or precursor for generation of model oxidized iron porphyrin compounds.

Electrochemical oxidation of $[FeTPP]_2O$ was carried out at 1.03 V (second cyclic voltammetry wave, reversible) vs. aqueous saturated calomel (SCE) in methylene chloride solvent using a tetraalkylammonium perchlorate salt as the supporting electrolyte.[3] Elemental analysis of the isolated solid was consistent with formulation as the bis perchlorate salt. The product was shown, by electron exchange with the parent iron(III) dimer, to possess two oxidation equivalents. Figure

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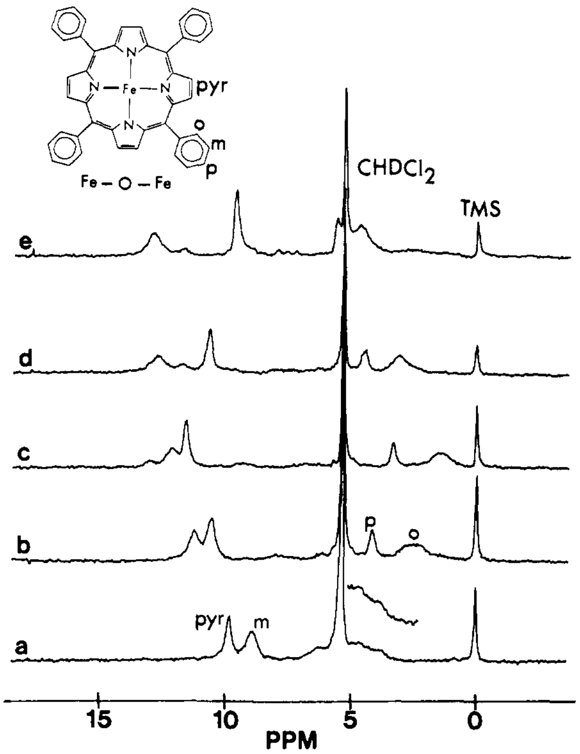

Figure 1. ^1H NMR titration of $[(FeTPP)_2O](ClO_4)_2$ by $(FeTPP)_2O$, oxidized dimer originally 5 mM in 0.5 mL of CD_2Cl_2, 26 °C. Moles of $(FeTPP)_2O$ added (× 10^6): (a) 0.0, (b) 1.05, (c) 2.50, (d) 3.91, (e) 5.00.

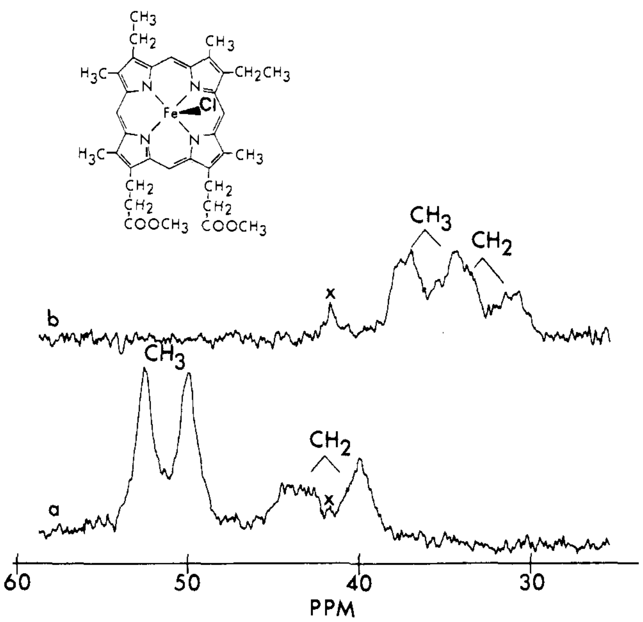

Figure 2. ^1H NMR of downfield ring methyl/methylene region for FeMPDME·Cl species, 5 mM in CD_2Cl_2, referenced to Me_4Si, 26 °C: (a) FeMPDME·Cl, (b) one-electron oxidation product of FeMPDME·Cl. X designates impurity present in both species.

1 describes titration of the bis oxidized dimer to the mixed oxidation state dimer as monitored by ^1H NMR in CD_2Cl_2 solvent.[4] The pyrrole and meta phenyl resonances are found at 9.8 and 8.9 ppm, respectively, whereas the ortho and para phenyl signals are seen at an upfield position in the doubly oxidized compound (Figure 1a). Upon addition of iron(III) titrant (Figures 1b and 1c) the pyrrole and meta resonances progress downfield and the ortho and para phenyl resonances upfield. Owing to rapid intra- and intermolecular electron transfer on the ^1H NMR time scale, only an averaged spectrum is observed. In this limit of fast exchange, the observed resonances are a mole fraction weighted average of the shifts for doubly and singly oxidized species. Figure 1c is that for the singly oxidized dimer. This mixed oxidation state dimer spectrum has been reproduced with the product obtained by direct electrochemical oxidation of the iron(III) dimer at the first cyclic voltammetric wave (0.79 V vs. SCE, reversible). Additional titration of the mixed oxidation state dimer with the iron(III) dimer gives rise to resonances which are the mole fraction weighted average (Figures 1d and 1e). With titration, ortho, meta, and para phenyl resonances move toward 7.6 ppm where they appear in the iron(III) dimer. Similarly, the pyrrole resonance approaches 13.6 ppm.

For the mixed oxidation state dimer the ortho and para phenyl proton signals are shifted upfield, and the meta signal is shifted downfield.[5] The para proton resonance has been assigned by oxidation of the *p*-methoxy-substituted derivative (oxidation potentials 0.68 and 0.86 V vs. SCE, reversible). ^1H NMR spectra and titrations resemble those for $[(FeTPP)_2O]^{2+}$ with the para proton signal absent. The ortho resonance was assigned by comparison of line widths. Variable-temperature ^1H NMR of the two-electron oxidation product reveals small resonance shifts, consistent with strong antiferromagnetic coupling of the two paramagnetic centers via the μ-oxo bridge. The meta resonance shows splitting into a doublet at 275 K, demonstrating the out-of-plane character of the iron atom. Visible spectra of these compound are very similar to those reported by Felton et al.[2]

The oxidized dimers can be cleaved by acid to give monomeric oxidized species. The monomeric $FeTPP·Cl^+$ species in CD_2Cl_2 generated by stoichiometric HCl addition to $[(FeTPP)_2O]^{2+}$ is equivalent to the product prepared by direct electrolysis (^1H NMR spectra of direct electrolysis product: pyrrole, 66.1; ortho, 37.6, 34.4; meta, −12.4; para, 29.5 ppm at 299 K[6]). Products in each case are reducible by tetrabutylammonium iodide titration. Oxidized materials show cyclic voltammetry waves identical with that of the parent iron(III) porphyrin. This indicates that, although the exact electronic nature of the oxidized dimers and monomers need not be the same, they do contain the same number of oxidizing equivalents per porphyrin unit.

Preliminary work involving the oxidation of other ferric porphyrins has been carried out using the oxidized FeTPP derivatives as chemical oxidants. Oxidation of iron(III) mesoporphyrin dimethyl ester chloride, FeMPDME·Cl, at its first cyclic voltammetry wave is possible with $[(FeTPP)_2O](ClO_4)_2$. Figure 2a shows the downfield ^1H NMR spectrum of FeMPDME·Cl, and 2b that of the oxidized species. Titration of oxidized material with the parent iron(III) porphyrin revealed averaged spectra as demonstrated above for the dimeric compounds. Iodide reduction likewise regenerated the iron(III) prophyrin. The slight shift in methyl and methylene resonances upon oxidation follows upfield shifts also observed for corresponding pyrrole substituents of oxidized iron octaethylporphyrin and iron etioporphyrin I species. Downfield isotropic shifts for both pyrrole protons and for ring methyl/methylene groups is indicative of single electron occupation of the $d_{x^2-y^2}$ orbital.[7] Morishima and Ogawa have reported ^1H NMR spectra for compounds I and II of horseradish peroxidase.[8] Large downfield isotropic shifts were observed for ring methyl and methylene groups of compound I and for the ferric enzyme. Shifts were somewhat smaller for compound I much as is the case for FeMPDME·Cl vs. the singly oxidized product.

Magnetic measurements could not be carried out on the oxidized FeMPDME·Cl monomer owing to the presence of paramagnetic oxidant. However, Evans method[9] measurements on $FeTPP(p\text{-}OCH_3)·Cl(ClO_4)$ in CD_2Cl_2 reveal a magnetic moment of 4.9 μ_B which is invariant over the temperature range 200–298 K. Although this is the expected magnetic moment for high-spin iron(IV), the formal oxidation state assignment is not proven. Thus, an alternate formulation could involve abstraction of the electron from a porphyrin-centered MO with subsequent strong coupling of iron(III) and the radical spins. This would leave a total of four unpaired electrons with electronic relaxation rates such that resolvable NMR signals might be expected. Such strong exchange coupling is apparent for copper(II) porphyrin π-cation radicals, which, as a result, exhibit a singlet ground state.[10] The site of iron porphyrin oxidation has not been elucidated, although some radical character of A_{2u} symmetry (large spin density at meso positions and little at β-pyrrole carbons) would serve to explain the unusually large phenyl proton isotropic shifts of oxidized FeTPP compounds.

Additional physical measurements are in progress using model compounds generated from doubly oxidized μ-oxo-bridged iron porphyrin dimers.

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(3) Cyclic voltammetry waves for the isolated product were identical with those of the iron(III) dimer, thus indicating no irreversible porphyrin modification. The oxidized product was also reducible by iodide titration. The possibility that these species are simply monomeric iron(III) porphyrin perchlorates is ruled out by a comprehensive ^{1}H NMR study of $Fe^{III}TPP{\cdot}ClO_4$: Goff H.; Shimomura, E., submitted for publication.

(4) ^{1}H NMR spectra were recorded at 90 MHz using a Bruker HX-90E instrument operating in the pulsed Fourier transform mode. The oxidized species were stable for longer periods of time than required for the ^{1}H NMR experiments as verified by separate experiments.

(5) Phenyl resonance assignments in ref 2 are reversed with respect to those reported here. Assignment by integration was complicated by availability of instrumentation with adequate sensitivity at the time of the earlier study.

(6) Assignments were made by titration with $Fe^{III}TPP{\cdot}Cl$ and concomitant monitoring of averaged signals. The para proton signal was readily assigned by evaluation of the $FeTPP(p\text{-}OCH_3){\cdot}Cl)^+$ spectrum. The discrepancy between resonances observed for our oxidized product and those given in ref 2 can be accounted for by differences in temperature, solvent, and the likelihood that considerable unoxidized material was present in the earlier preparations. Likewise the optical spectrum of $FeTPP{\cdot}Cl(ClO_4)$ resembles that reported in ref 2, and an identical spectrum may be generated if some iron(III) material is added to the product.

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Kinetics of Penetration of a Probe Molecule into a Reversed Micelle

Sir:

Surfactant aggregates in apolar solvents, termed reversed micelles, have been the subject of recent increasing interest[1-5] owing to their industrial applications and to their ability to mimic biological membranes. Reversed or inverted micelles can be characterized as aggregates of surfactant molecules with their polar groups concentrated in the interior of the aggregate while their hydrophobic groups extend into and are surrounded by the bulk apolar solvent. They are capable of solubilizing a considerable amount of water and other polar molecules.[2-5]

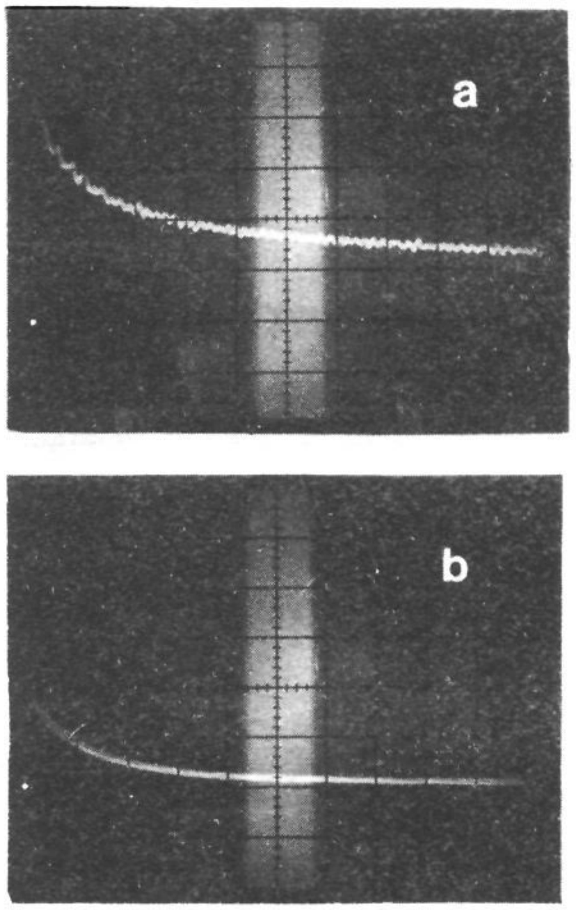

Figure 1. Time courses of a concentration-jump experiment carried out by mixing 2×10^{-5} M picric acid and 2×10^{-3} M Aerosol-OT solutions in benzene at 25 °C. Vertical scale: transmitted light intensity in arbitrary unit. Abscissa: (a) 20 ms/division; (b) 0.5 s/division. Wavelength of observation: 420 nm.

While there is a considerable accumulation of experimental results available about reversed micellar systems, as well as on their catalytic effects,[6] the information is incomplete. An unambiguous quantitative interpretation of micellar behavior is still missing. Even the basic concepts of the systems, such as the existence of critical micelle concentration (cmc), as well as the kinds of aggregates existing in solution, have been the object of controversy.[1,7-9] Especially much work is needed on the dynamic behavior of reversed micelles,[10] investigating the kinetics of their formation, and the solubilization of other molecules by the aggregates.

In the present communication we present kinetic results on the penetration of a probe molecule, picric acid, into reversed micelle of Aerosol-OT (di-2-ethylhexylsodium sulfosuccinate) in benzene containing 0.03% water. Aerosol-OT is a typical anionic surfactant forming reversed micelle in apolar solvent, the mean aggregation number of which is reported to be constant in a wide concentration range.[1,11] Picric acid is colorless in benzene, but it shows two characteristic absorption peaks at λ 345 and 420 nm in the presence of Aerosol-OT. The spectrum is similar to that of picric acid in water. The color change is apparently due to the dissociation of the indicator in and/or at the water pool of the micelle.

To investigate the rate of penetration of the indicator into the micelle, concentration- and solvent-jump[12] experiments were carried out using a stopped-flow apparatus that has already been described.[13] In a typical concentration-jump experiment the Aerosol-OT micellar solution (the surfactant concentration ranging from 2×10^{-4} to 1.6×10^{-2} M) was rapidly mixed (in 1 ms) with a benzene solution of picric acid (2×10^{-5} M) at a volume ratio of 1:1 at 25 °C. By monitoring the color change at λ 420 nm, two distinct rate processes can be observed. Representative oscilloscope traces are shown in Figure 1. Each of the rate processes was analyzed by fitting the curve to an exponential function. The time constant τ_1^{-1} of the faster process increases with the surfactant concentration until it reaches a constant value of 36 s^{-1} above 5×10^{-4} M Aerosol-OT. On the other hand, the time constant τ_2^{-1} of the slower reaction increases almost linearly from 0.9 to 2.8 s^{-1} with the

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