in EPA raises the fluorescence quantum efficiency for 3,3′BPE to unity.

The remaining isomeric 1,2-bispyridylethylenes and 2- and 4-stilbazole show behavior similar to that of 4,4′BPE on direct irradiation; fluorescence yields are low,[6] and decay *via* a lower energy ^{1}n,π^* state is suggested by photoreduction reactions and/or low cis–trans isomerization efficiencies. The only azastilbene behaving similarly to 3,3′BPE is 3-stilbazole, which, like 3,3′BPE, has nitrogen only in a position meta to the ethylenic linkage. CNDO and INDO calculations suggest that nitrogen location causes little difference in energies of n,π^* excited states for isomeric stilbazoles and 1,2-bispyridylethylenes.[11,12] However, both the highest bonding π MO's as well as the lowest antibonding π MO's of stilbene and the azastilbenes (those involved in π,π^* excitation) have near nodes at the 3 or meta position (coefficients from HMO calculations on stilbenes: π, 0.079; π^*, 0.079;[13] these are similar to coefficients from CNDO and INDO calculations).[12] The location of nitrogen at a near node in the π MO may possibly render the n,π^* excited states inaccessible from the initially formed $^1\pi,\pi^*$ state. Rates of radiationless decay are predicted to depend on an electronic integral between the initial and final states;[14] therefore, it is reasonable that for N-heterocycles with nitrogen at a near node in the π MO, the electronic integral $\beta_{\text{el}} = \langle\psi_{\pi,\pi^*}|H'|\psi_{\text{n},\pi^*}\rangle$[14] is small enough to reduce rates of radiationless interconversion.[15,16]

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[15] To test the hypothesis, we have carried out INDO calculations on the 1-, 2-, and 3-azaphenanthrenes (nitrogen occurs at a near node in 2-azaphenanthrene). While the results are not as gratifying as hoped, the direction of fluorescence yields is roughly in line with the hypothesis. Since several additional factors could influence both radiationless decay as well as fluorescence yields (*e.g.*, vibronic coupling, lifetime of the ^{1}n,π^* state, and reversible population of the $^1\pi,\pi^*$ state), it is not at all clear that a quantitative correlation would be expected.

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Iron(IV) Porphyrins

Sir:

Tetravalent heme iron has been evoked[1] to explain the course of oxidation in catalase, horse radish peroxidase, and cytochrome-*c* peroxidase. Recently it was proposed[2] that the catalytically active primary compounds of catalase and horse radish peroxidase are π-cation radicals of Fe(IV) porphyrins. We now show that stable, one-electron oxidation products of ferric porphyrins can be prepared, and that the oxidation is best characterized as electron abstraction from the metal in contrast to removal of an electron from the porphyrin π system.

Cyclic voltammetry of tetraphenylporphyrin iron(III) chloride, FeTPPCl, or octaethylporphyrin iron(III) chloride, FeOEPCl, in dichloromethane–tetrapropylammonium perchlorate (TPAP) solutions showed reversible one-electron oxidation to occur at $\epsilon_{1/2}$ = 1.13 and 0.99 V *vs.* sce (aqueous), respectively. One-electron, reversible half-wave potentials at $\epsilon_{1/2}$ = 0.84 and 1.09 V were observed for the dimer, μ-oxo-bis(tetraphenylporphyrin iron(III)),[3] $(\text{FeTPP})_2\text{O}$, and at $\epsilon_{1/2}$ = 0.66 and 0.96 V for μ-oxo-bis(octaethylporphyrin iron(III)), $(\text{FeOEP})_2\text{O}$.

Controlled potential electrolyses of the ferric porphyrins were carried out at the plateau of their first oxidation wave. Spectral changes occurring during oxidation are shown in Figures 1 and 2. Simultaneous coulometry indicated that one-electron oxidations had taken place: 1.0 ± 0.1 electron per FeTPPCl or FeOEPCl, or per $(\text{FeTPP})_2\text{O}$ or $(\text{FeOEP})_2\text{O}$ dimer. The parent iron(III) porphyrins were recovered in yields exceeding 95% by either electrochemical or iodide reduction. In CH_2Cl_2 the oxidized ferric porphyrins decay at a rate of a few per cent per hour. The oxidized $(\text{FeTPP})_2\text{O}$ was isolated in crystalline form as the perchlorate salt (ClO_4^- ir absorptions[4] at 1090 and 620 cm^{-1} in KBr) by washing the solid isolated from the electrolysis with boiling water to remove TPAP and then with benzene to remove the parent compound. The crystalline solid $(\text{FeTPP})_2\text{O}^+,\text{ClO}_4^-$ redissolved in CH_2Cl_2 exhibited a polarographic reduction potential of 0.84 V and a spectrum identical with that of Figure 2, thus demonstrating that no change had occurred during isolation. The presence of positive charge was established by a moving boundary experiment performed as previously described.[5]

The pmr spectrum of $(\text{FeTPP})_2\text{O}$ was compared with that of the isolated oxidized material. In the former compound two resonances were observed: a broad (~50 Hz) signal at 13.6 ppm downfield from TMS[6] and a resonance at 7.6 ppm with width ~20 Hz. Relative intensities are 1:2.5, and we assign[7] them to β-pyrrole and phenyl protons, respectively. At 40° the oxidized dimer in CDCl_3 displayed absorptions (widths) at 3.4 (~25 Hz), 11.4 (~25 Hz), and 12.2 ppm (~50 Hz). Relative intensities are approximately 1:1.5:1. As the concentration ratio of oxidized porphyrin to parent porphyrin was decreased by addition of iodide, the 11.4- and 3.4-ppm lines coalesced into the 7.6-ppm resonance of $(\text{FeTPP})_2\text{O}$, and the 12.2- ppm resonance moved to 13.6 ppm. The pmr spectra are consonant with a fast electron exchange between $(\text{FeTPP})_2\text{O}^+$ and $(\text{FeTPP})_2\text{O}$ giving rise to a number-averaged spectrum. In accord with these data, the following assignments of the $(\text{FeTPP})_2\text{O}^+$ lines are made: β-pyrrole protons,

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[6] Resonances were measured relative to internal CHCl_3 and are cited with respect to an internal TMS standard.

[7] The assignments agree with those reported by P. D. W. Boyd and T. D. Smith, *Inorg. Chem.*, 10, 2041 (1971).

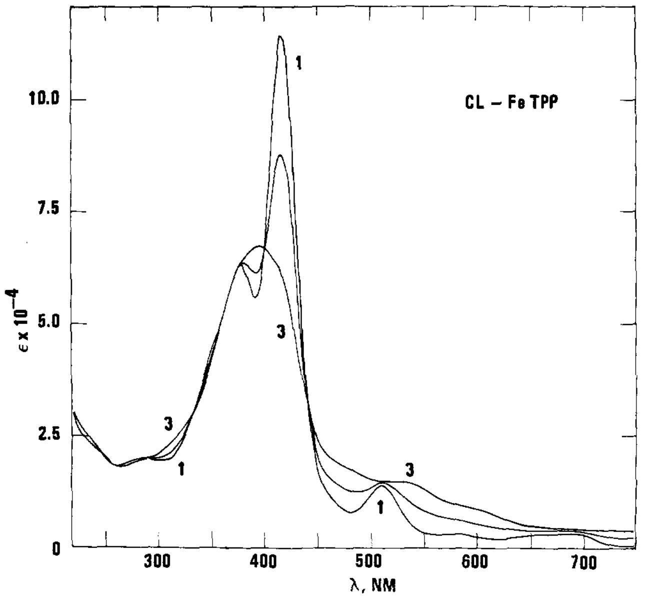

Figure 1. Spectral changes occurring during electrochemical oxidation of FeTPPCl in CH_2Cl_2: 1, FeTPPCl; 2, intermediate state of oxidation; 3, $FeTPPCl^+$.

12.2 ppm; ortho and para phenyl protons, 11.4 ppm; and meta phenyl protons, 3.4 ppm. The phenyl proton assignments are supported by prior experiments[8] which show that contact shifts of ortho and para phenyl protons are opposite to those of meta phenyl protons.

The following evidence suggests that $(FeTPP)_2O^+$ is not a porphyrin π-cation radical: (1) the optical changes occurring upon oxidation are not typical of π-cation porphyrin radicals which show[9] strongly enhanced absorption from 500 to 700 nm; (2) comparison of the polarographic oxidation potentials of the chloro monomers with those of the oxo dimers is consistent with the increased ease of oxidation of iron in the dimers being caused by binding to the electronegative oxo group; the two polarographic waves in the dimers are interpretable as stepwise oxidation of each iron, and, most importantly; (3) the $(FeTPP)_2O^+$ pmr resonances are shifted by not more than 4 ppm from the corresponding $(FeTPP)_2O$ resonances. If the porphyrin ring had been oxidized, then based upon an observed[9] hyperfine splitting constant of 0.3 G for the π-cation radical of zinc tetraphenylporphyrin, phenyl contact pmr shifts of approximately 40 ppm would be anticipated.[8] The possibilities that one ring of the dimer is oxidized with occurrence of either (a) fast or (b) slow exchange with the unoxidized ring are ruled out by the pmr data. Thus in case (a) phenyl pmr shifts of 20 ppm from the corresponding $(FeTPP)_2O$ resonance would be predicted. In case (b) the total pmr spectral intensity would double when all of the oxidized material was reduced (protons on both rings would now contribute to the pmr spectrum); in fact, no change in the signal intensity occurs with reduction.

The pmr spectrum of oxidized FeTPPCl displays only small shifts when compared to that of FeTPPCl. In $CDCl_3$ a 9:1 mixture of oxidized and parent FeTPPCl displayed broad resonances at 12.3 and 5.8 ppm. In chloroform $FeTPPCl^+$ is much less stable than $(FeTPP)_2O^+$, and the parent FeTPPCl was recovered after a period of a few hours. During this time the 12.3-ppm peak had progressed to 6.5 (phenyl protons) and the 5.8-ppm peak to 12.5 (phenyl protons). In a separate experiment, a CH_2Cl_2 solution containing greater than 90% $FeTPPPCl^+$ showed a broad absorption at 68.6 ppm (β-pyrrole protons) which, in time, progressed to 79.4 ppm. (Pmr assignments are based upon a previous study.[10]) Nmr susceptibility measurements using the technique of Evans[11] with careful attention to density corrections showed that $FeTPPCl^+$ in CH_2Cl_2 had[12] a spin of $S = 2$, whereas $S = {}^5/_2$ for FeTPPCl.

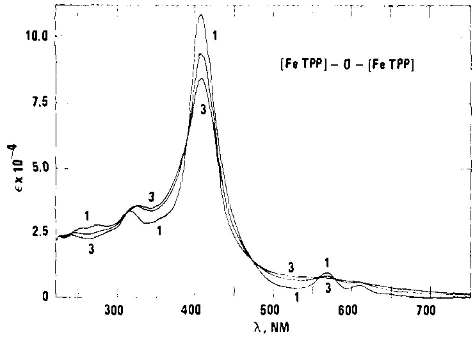

Figure 2. Spectral changes occurring during electrochemical oxidation of $(FeTPP)_2O$ in CH_2Cl_2; numbering of spectra as in Figure 1. The extinction coefficient is given per iron.

As in the case of the oxidized dimer, these data imply that one-electron oxidation of the monomer does not result in removal of an electron from a porphyrin π orbital. The molecular orbital calculations of Zerner, Gouterman, and Kobayashi[13] on high-spin ferric porphyrin complexes show that the highest occupied orbital is b_{1g} (D_{4h}) which consists of contributions from the iron $d_{x^2-y^2}$ orbital (46%) and the nitrogen σ orbitals (four nitrogens totaling 46%). The next occupied orbital, a_{1g}, lies at least 1.3 eV lower. Using their program we find that this ordering is unchanged in the oxidized ferric porphyrin. Thus we suggest that $FeTPPCl^+$ is formed by electron abstraction from the b_{1g} orbital of FeTPPCl and contains iron in a formal 4+ oxidation state in the same sense that 3+ and 2+ are the formal oxidation states in hemes. The value of $S = 2$ for the oxidized porphyrin is consistent with this view. Although no calculations have been reported for the μ-oxo-ferric porphyrin dimers, the oxidation might be viewed as electron removal from a molecular orbital extending over the FeOFe region with some contributions from nitrogen σ orbitals.

These results provide evidence for the existence of Fe(IV) porphyrins. The relationships between these compounds and the primary and secondary compounds of catalase and peroxidase are under investigation.

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Acknowledgment. We wish to thank Dr. D. C. Borg for helpful discussions and Professor M. Gouterman for a copy of the Zerner-Gouterman extended Hückel program. This work was supported by the National Institutes of Health and National Science Foundation (Grants No. AM14344 and GP17061 at Georgia Institute of Technology and AM14343 at Harvard), and by the U. S. Atomic Energy Commission at Brookhaven National Laboratory.

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Accurate Relative Acidities in the Gas Phase. Hydrogen Sulfide and Hydrogen Cyanide[1]

Sir:

Solution studies of acid–base equilibria have elucidated a number of structural and electronic effects which influence the acid strength of molecules. It is well known, though, that the nature of the solvent can also have a significant effect on acidity.[2] This phenomenon has been demonstrated in a striking manner recently by studies which have shown that the acid strength of molecules in the gas phase is often quite different from that observed in solution.[3,4] For example, Brauman and Blair have reported that in the gas phase toluene is a stronger acid than water and *tert*-butoxide is less basic than methoxide.[3b] Since ions are not solvated at the low pressures used in these gas-phase experiments, the intrinsic acidity of molecules can be determined in the absence of solvent effects.

Using conventional ion cyclotron resonance (icr) techniques, Brauman and Blair were able to determine relative orders of gas-phase acidity. In this communication we demonstrate that similar systems can be studied in a quantitative manner using the pulsed icr equilibrium technique. The equilibrium constant for the gas-phase reaction

$$SH^- + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CN^- + H_2S \tag{1}$$

is measured for the first time, and special efforts are made to demonstrate that equilibrium is being attained in this system. Equilibrium icr techniques were first used by Bowers, Aue, Webb, and McIver to determine accurate relative proton affinities for a series of amines, and a significant advantage of this new method is that thermochemical values can be measured to an accuracy of ±0.2 kcal/mol, almost an order of magnitude more accurate than previously available values.[5]

The pulsed icr technique has been described previously.[6] Gaseous ions are formed by a short pulse of an electron beam and then trapped in an analyzer cell by the combined effects of magnetic and electrostatic fields. The ions can be trapped efficiently for periods as long as 1 sec, and at any time during the trapping period the ions present in the analyzer cell can be mass analyzed.

Figure 1 shows typical experimental data used to determine the relative gas-phase acidity of H_2S and HCN. One of the dual sample inlets on the pulsed icr spectrometer was used to add an H_2S–HCN mixture of known composition to a pressure of 1×10^{-6} Torr, while the other inlet was used to add NF_3 to a total pressure of 2×10^{-6} Torr. Fluoride ion is formed efficiently from NF_3 by low-energy electron impact: $NF_3 + e^- \rightarrow F^- + NF_2\cdot$.

The upper trace in Figure 1 shows that a 5-msec pulse of the electron beam produces a large initial concentration of F^- which decays exponentially as it reacts with H_2S and HCN. The F^- rapidly abstracts a proton from H_2S and HCN because it is a stronger base than SH^- or CN^-. The middle trace in Figure 1 shows that the CN^- concentration increases gradually and then levels off to a constant value after about 200 msec. The SH^- concentration rises rapidly with a peak at 50 msec and then decays gradually to a constant equilibrium value.

An examination of the traces in Figure 1 suggests that equilibrium is being attained in the H_2S–HCN system. The reactants do reach constant concentrations after reacting for 300 msec, and the concentration of SH^- first increases and then decreases as if the reverse reaction were occurring to bring the system back to equilibrium. Experiments of this type give $K = 9.0 \pm 0.6$ for the equilibrium constant of reaction 1.[7] Additional experiments were performed, however, to test further whether equilibrium is in fact being attained.

The traces labeled A in Figure 2 were obtained in the same manner as the ones in Figure 1 except that an H_2S–HCN mixture of different relative composition was used. The equilibrium concentration of the ions gives $K = 9.1$, in good agreement with the result obtained above. The equilibrium constant can also be determined by measuring the rate constants, k_1 and k_2, for the forward and reverse reactions: $K = k_1/k_2$. Ejection of either CN^- or SH^- from the analyzer cell using strong double-resonance irradiation[8] perturbs the system, and the rate at which the system responds to the perturbation is determined by the rate of the forward or reverse reaction.[9] Trace B in the upper half of Figure 2 shows that the concentration of CN^- is significantly altered when SH^- is totally ejected from

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(7) $K = (I_{CN^-}/I_{SH^-})(26/33)([H_2S]/[HCN])$, where I_{CN^-} is the intensity of the CN^- signal; 26 the mass of CN^-, a mass correction factor; and [HCN] the pressure of HCN in the system.

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