be prepared in high yields from HF solutions and have been known for 80 years or longer. As in the cases of noble gas[20] or NF_4[21] chemistry, the successful chemical synthesis of elemental fluorine demonstrates that one should never cease to critically challenge accepted dogmas.

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Electrochemical Generation of Iron(IV)-Oxo Porphyrins and Iron(IV)-Oxo Porphyrin π Cation Radicals

Sir:

With weakly basic ligands, such as chloride or perchlorate, the first electrochemical 1e oxidation of an iron(III)porphyrin is porphyrin-centered, resulting in the formation of an iron(III)-porphyrin π cation radical.[1] We were the first to show[2,3] that when the ligands are the strongly basic oxy anions, HO^- and CH_3O^-, the first electrochemical 1e oxidation is iron-centered, providing an iron(IV) porphyrin. In our investigations (dry CH_2Cl_2 solvent), potentials were determined by cyclic voltammetry, coulometry was determined by controlled-potential oxidation at the potentials corresponding to the CV peak positions, and the nature of the products was established by low-temperature spectroelectrochemistry and comparison of the spectra to those of known porphyrin species. In addition, the identification of electrochemically generated iron(IV) porphyrin species was verified by chemical conversion to known species at the same oxidation level. To obviate μ-oxo dimer formation all investigations employed (*meso*-tetrakis(2,6-disubstituted phenyl)porphinato)iron(III) hydroxide and methoxide salts. In this manner, we showed that (tetrakis(2,4,6-trimethylphenyl)porphinato)iron(III) hydroxide ($(TMP)Fe^{III}OH$) on 1e oxidation (+1.01 V)[4] provides an iron(IV) porphyrin ($(TMP)Fe^{IV}O$),[5] and the second 1e oxidation (+1.13 V) gives an iron(IV) porphyrin π-cation radical ($({}^{\bullet+}TMP)Fe^{IV}O$).

In a recent communication in this journal, Groves and Gilbert reexamined the electrochemistry of $(TMP)Fe^{III}OH$ in wet CH_2Cl_2 saturated with Na_2CO_3.[6] Their results substantiated our original discovery that the first and third oxidation peaks observed with $(TMP)Fe^{III}OH$ are for the formation of $(TMP)Fe^{IV}O$ and $({}^{2+}TMP)Fe^{IV}O$, respectively, but disputed the value of our second oxidation potential for the formation of $({}^{\bullet+}TMP)Fe^{IV}O$. The two 1e oxidation potentials that they report are +1.01 and +1.40 V. They attributed our results to the presence of chloride ion impurity and to the absence of Na_2CO_3 and water. We show here that chloride ion is not present in our system; we provide additional data in support of our assignment of potentials for 1e oxidation of iron(IV) porphyrins to the corresponding iron(IV) porphyrin π cation radicals; and we show that the potential (+1.01 V)[6] assigned by Groves and Gilbert for the 1e oxidation of $(TMP)Fe^{III}OH$ to $(TMP)Fe^{IV}O$ is in actuality due to two 1e oxidations.

The following observations establish the absence of all chloride ion. In our experiments pure $(TMP)Fe^{III}OH$ was used and the solvent and electrolyte system was devoid of chloride ion. Reactions were carried out at −71 °C where CH_2Cl_2 solvent does not undergo oxidation. In Figure 1 there is shown repetitive visible spectral scans of the first two sequential 1e oxidations of $(TMP)Fe^{III}OH$ (conditions, positions of isosbestic points, peak heights, etc. provided in the caption). That the spectral changes of parts A and B of Figure 1 are associated with 1e oxidations follows from their generation by controlled-potential coulometry. From the isosbestic points there is seen to be no competitive change of ligand nor accumulation of intermediate. Inspection of Figure 1A reveals the absence of the spectral characteristics (absorbance at 380 and 510 nm) of $(TMP)Fe^{III}Cl$. Indeed, spectroelectrochemistry at −71 °C with $(TMP)Fe^{III}Cl$ shows that 1e oxidation at 1.18 V is accompanied by a decrease in the Soret absorbance at 420 nm and an increase in absorbance at 398 nm with an isosbestic point at 528 nm. Additional evidence for the absence of chloride ion in our experiments is shown by the observation that the presence of trace concentrations (10^{-5}–10^{-4} M) of $[(n\text{-}C_4H_9)_4N^+][Cl^-]$ in a solution of $(TMP)Fe^{III}OH$ results in a CV where the first oxidation is no longer reversible. Such is not the case with the CV's we have reported.[2,3] It is known[7] that the reduction of iron(III) porphyrin to iron(II) porphyrin is strongly influenced by the axial ligand. Employing $(TMP)Fe^{III}OH$, we find that the 1e-reduction potential is at −1.05 V while the potential for 1e reduction of $(TMP)Fe^{III}Cl$ occurs at −0.75 V (dry CH_2Cl_2, 25 °C). The samples of $(TMP)Fe^{III}OH$ employed in the electrochemical and spectroelectrochemical studies showed no evidence of a peak potential at −0.75 V. In our hands the electrochemical oxidations of $(TMP)Fe^{III}OH$ have been found to be both chemically and electrochemically reversible.

Groves and Gilbert (working in a solvent composed of CH_2Cl_2 wet with water and saturated with Na_2CO_3) reported that the oxidation of $(TMP)Fe^{IV}O$ to $({}^{\bullet+}TMP)Fe^{IV}O$ is irreversible and occurs at a higher potential (+1.40 V) than the potential (+1.14 V) for the $(TMP)Fe^{III}Cl$ to $({}^{\bullet+}TMP)Fe^{III}(Cl)_2$ oxidation. A CV similar to theirs, with the exception of the absence of the irreversible peak at +1.40 V, is obtained for $(TMP)Fe^{III}OH$ in CH_2Cl_2 that has been wet by being passed through air-equilibrated alumina (Figure 2A). By simple visual observation of the CV, it might appear as though the first oxidation wave (1.01 V) represents a single 1e process, as they assumed. Controlled-potential coulometry (at 1.06 V) at −71 °C showed that there are two electrons ($n = 2.1 \pm 0.2$) associated with this wave. For the low-temperature controlled-potential coulometry, the system was first calibrated by using $(TMP)Fe^{III}Cl$. The coulometric oxidation was monitored by change of current measurement with time and also by running a CV when n is equal to 1. Therefore, the first oxidation wave must represent two 1e oxidations that are so close in potential that they cannot be distinguished by CV.[8] A possible explanation for

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(4) All potentials given in this paper are vs. a saturated caromel electrode (SCE). The potentials given by Groves and Gilbert are corrected to SCE by using the conversion factor in their paper.

(5) The nature of the oxo ligand is not known. Though the iron(IV)-oxo porphyrin is written as $(TMP)Fe^{IV}O$, the oxo ligand may be −OH or perhaps a second oxo ligand may be present since it is virtually impossible to free a polar organic solvent of all traces of water. In our previous publications (ref 2 and 3), we used the notation $(TMP)Fe^{IV}OH$.

(6) Groves, J. T.; Gilbert, J. A. *Inorg. Chem.* **1986**, *25*, 123–125.

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(8) There is no reason that two 1e oxidations so close in potential should resemble a 2e oxidation with CV. Bard and Faulkner (Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 233–235) point out that when the potential difference between two 1e processes is less than 100 mV the individual waves are merged into a broad wave. Also, they show that if the difference is 35.6 mV (theoretical), which occurs when there is no interaction between the redox groups on the substrate, then the observed wave has all the characteristics of a 1e transfer.

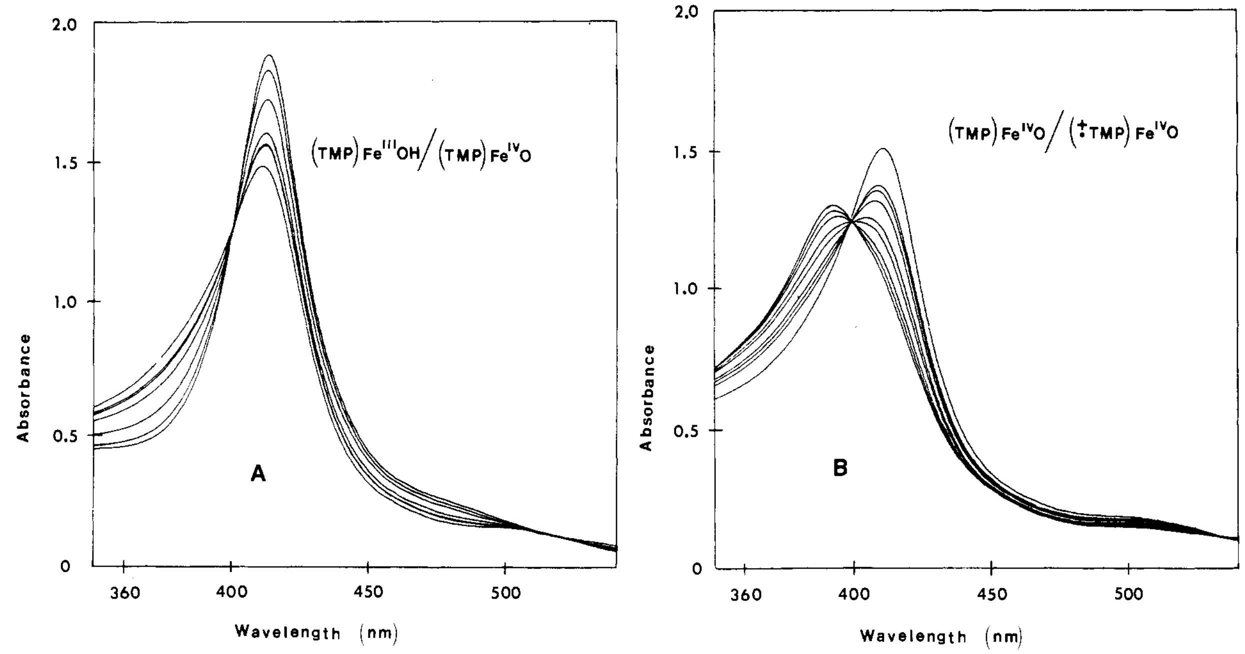

Figure 1. Visible spectral scans at −71 °C in dry CH_2Cl_2 of the sequential 1e oxidations of 2.06 × 10^{-4} M (TMP)Fe^{III}OH to (TMP)Fe^{IV}O (part A) and ($^{\bullet+}$TMP)Fe^{IV}O (part B). Conversion of (TMP)Fe^{III}OH to (TMP)Fe^{IV}O is associated with a shifting of the Soret band from 415 to 412 nm and loss of the 580-nm band (characteristic of hydroxide ligation to iron(III) porphyrin) with isosbestic points at 400, 515, and 620 nm. The oxidation was carried out at 1.03 V until the coulometric count was equal to 1e (the charging current has been subtracted out in all experiments). Conversion of (TMP)Fe^{IV}O to ($^{\bullet+}$TMP)Fe^{IV}O is associated with the shifting of the Soret band from 412 to 392 nm and the appearance of a broad absorbances at 620 and 650 nm with isosbestic points at 399 and 534 nm. The oxidation was carried out at the fixed potential of 1.18 V. These experiments were carried out in a 1-mm spectroelectrochemical quartz-cuvette housing, from top to bottom and from wall to wall, a platinum-grid working electrode and two side compartments, one of which contained an Ag/AgCl reference electrode separated from the cuvette by a cracked bead tube and the second contained a platinum-flag auxiliary electrode separated from the cuvette by a medium glass frit. The solvent was Burdick and Jackson CH_2Cl_2 (purified and passed through vacuum-oven-dried alumina) with 0.1 M chloride-free (by electrochemistry) $(n\text{-}C_4H_9)_4N^+ClO_4^-$.

the observation by Groves and Gilbert of an irreversible wave at +1.40 V is that HO^- exhibits an irreversible oxidation around +1.40 V in CH_2Cl_2. The plausible presence of HO^- in their system could come about by their use of wet CH_2Cl_2 and the addition of Na_2CO_3. Balch[9] has provided evidence that the π cation radical ($^{\bullet+}$TMP)Fe^{III}ClO$_4$ reacts with (TMP)Fe^{IV}O to provide ($^{\bullet+}$TMP)Fe^{IV}O and (TMP)Fe^{III}ClO$_4$ and concluded that ($^{\bullet+}$TMP)Fe^{III}(ClO$_4$)$_2$ is at a higher oxidation potential than (TMP)Fe^{IV}O. This result shows that the oxidation potential of ($^{\bullet+}$TMP)Fe^{IV}O cannot be higher than that of ($^{\bullet+}$TMP)Fe^{III}(ClO$_4$)$_2$. Thus, the previous claim that the potential for 1e oxidation of (TMP)Fe^{IV}O is 200 mV higher than the 1e oxidation potential for (TMP)Fe^{III}Cl is not supported by the findings of Balch. (One should note that the potentials of iron(III) porphyrins ligated to Cl^- and ClO_4^- are identical.[1]) Figure 2B shows the CV of (TMP)Fe^{III}OH in CH_2Cl_2 at −71 °C. This CV clearly demonstrates that the system is reversible at low temperature.

In the study of the electrochemical epoxidation of norbornene in the presence of (TMP)Fe^{III}OH at +1.19 V, Groves and Gilbert assumed that the epoxidizing species is formed by the disproportionation of electrochemically generated (TMP)Fe^{IV}O to provide (TMP)Fe^{III}OH and the reactive ($^{\bullet+}$TMP)Fe^{IV}O. This assumption is baseless since in this single experiment they employed dry CH_2Cl_2 and we have shown[2,3] previously (loc. cit.) that in this solvent the potential for the formation of ($^{\bullet+}$TMP)Fe^{IV}O is at +1.13 V.

Our previous findings have been further supported by the study of (tetrakis(2,4,6-trimethoxyphenyl)porphinato)iron(III) hydroxide (TTMPP)Fe^{III}OH).[10] The methoxy substituents lower the oxidation potential of the iron(III) porphyrin ($E_{1/2}$ = 0.96 V for (TTMPP)Fe^{III}Cl as compared to $E_{1/2}$ = 1.13 V for (TMP)Fe^{III}Cl). By CV and controlled-potential coulometry the first 1e oxidation potential for (TTMPP)Fe^{III}OH is at +0.86 V. The visible spectra

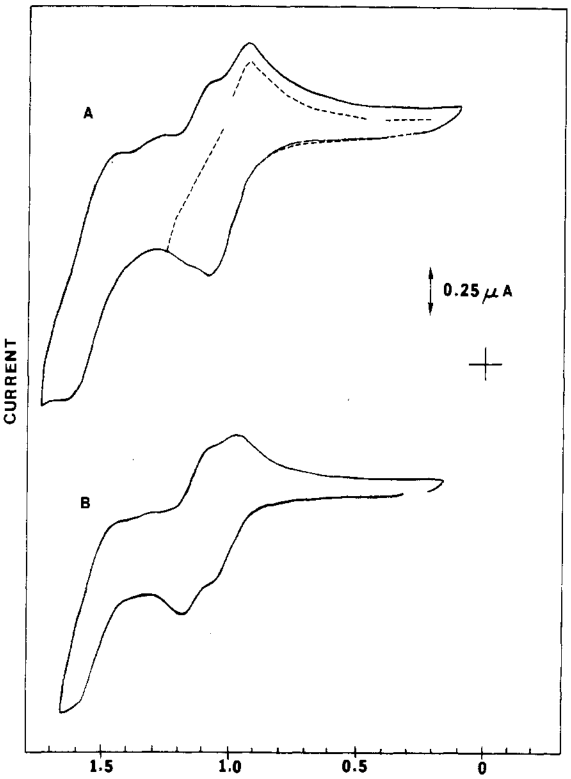

Figure 2. (A) Cyclic voltammogram of a 4.0 × 10^{-4} M solution of (TMP)Fe^{III}OH in CH_2Cl_2 (wet by passing through an air-equilibrated neutral alumina column) with 0.1 M chloride-free $(n\text{-}C_2H_9)_4N^+ClO_4^-$ as electrolyte. (B) Cyclic voltammogram of a 3.5 × 10^{-4} M solution of (TMP)Fe^{III}OH in dry CH_2Cl_2 (0.1 M $(n\text{-}C_2H_9)_4N^+ClO_4^-$) at −71 °C.

of (TTMPP)Fe^{III}OH and its 1e- and 2e-oxidation products, generated by controlled-potential coulometry at −71 °C, are shown

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[9] Balch, A. L.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2983–2985.

[10] Amudsen, A. R.; Vastra, L. *Inorg. Chim. Acta* **1975**, *14*, L49.

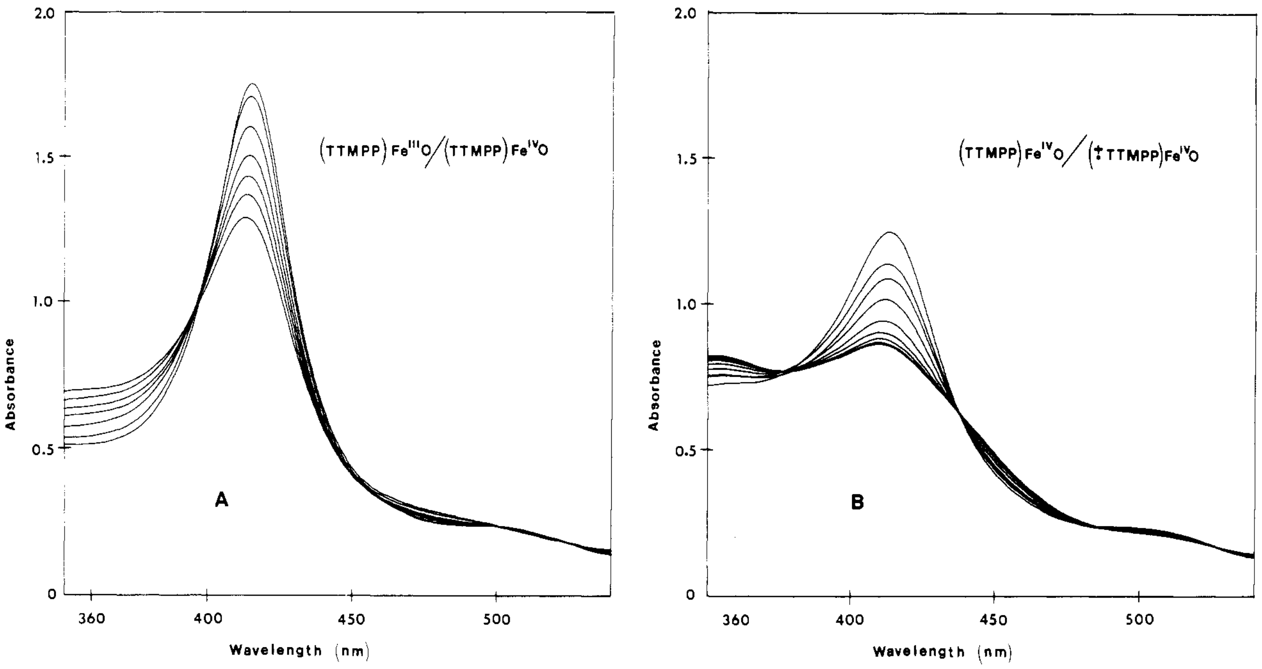

Figure 3. Visible spectral scans in dry CH_2Cl_2 of the first two sequential 1e oxidations of 1.63×10^{-4} M (TTMPP)$Fe^{III}OH$ to (TTMPP)$Fe^{IV}O$ and ($^{\bullet+}$TTMPP)$Fe^{IV}O$. The first electron transfer (part A) is associated with a shifting of the Soret band from 416 to 413 nm and the loss of the 580-nm band with isosbestic points at 397, 501, 524, and 620 nm. The oxidation was carried out at 0.90 V until the coulometric count was equal to 1e. The second electron transfer (part B) is associated with a decrease in the absorbance of the 413-nm band and the development of a Soret band at 353 nm and a broad absorbance at 620 nm with isosbestic points at 437 and 527 nm. The oxidation was carried out at 1.02 V. The apparatus and conditions are described in the caption to Figure 1.

in Figure 3A,B. Examination of Figure 3A shows that the first 1e oxidation results in a decrease in the absorbance of the Soret band (418 nm) without significant change in its position. The isosbestic points for the 1e oxidation of (TTMPP)$Fe^{III}OH$ indicate there are no visible intermediates, and the final spectrum is consistent with that of other iron(IV) porphyrin spectra such as the one generated from (TMP)$Fe^{III}OH$ by ourselves and later by Groves and Gilbert as well as the spectrum reported by Groves and co-workers[11] for (TMP)$Fe^{IV}(OCH_3)_2$. The second 1e oxidation of (TTMPP)$Fe^{III}OH$ results in a spectrum that has a Soret band at 353 nm, a shoulder at 415 nm, and an α,β-region absorbance at 620 nm. This spectrum closely resembles the visible spectrum of the π cation radical generated by 1e oxidation of (TTMPP)$Fe^{III}Cl$, which has its Soret band at 350 nm and secondary absorbances at 550 and 610 nm. This is not surprising since the Soret band is a property of the electron density of the porphyrin ring. The presence of iron(IV) in the cavity of the porphyrin ring has little effect on the Soret band, indicating that the oxidation is centered on the iron moiety. Because the electron density of the π system is not distrubed greatly by the presence of the iron(IV), it follows that the spectrum of ($^{\bullet+}$TTMPP)$Fe^{IV}O$ (λ_{max} 353 nm) should exhibit a close resemblance to that of ($^{\bullet+}$TTMPP)$Fe^{III}Cl$ (λ_{max} 350 nm). This is also observed in the spectrum (Figure 1B) of ($^{\bullet+}$TMP)$Fe^{IV}O$ (λ_{max} 398 nm). The chloroiron(III) porphyrin π cation radical and the oxoiron(IV) porphyrin π cation radical can be easily differentiated by their thermal stabilities. Thus, the species formed by 2e electrochemical oxidation of (TTMPP)$Fe^{III}OH$ (($^{\bullet+}$TTMPP)$Fe^{IV}O$) is completely decomposed to (TTMPP)$Fe^{III}Cl$ upon being warmed to −27 °C, while ($^{\bullet+}$TTMPP)$Fe^{III}Cl$ is fairly stable at room temperature. These results provide support for the position of the oxidation potential associated with the (TTMPP)$Fe^{IV}O$/($^{\bullet+}$TTMPP)$Fe^{IV}O$ couple. Thus, if the oxidation of iron(III) to iron(IV) has only a minimal effect on the electron density of the porphyrin ring, then it would be expected that the oxidation potential for the formation of the π cation radical should be approximately the same regardless of whether there is an iron(III) or iron(IV) in the cavity. As observed[2] for a number of other sterically blocked and hydroxy-ligated iron(III)porphyrins, the first 1e oxidation potential for (TTMPP)$Fe^{III}OH$ lies 100 mV below that of the first 1e oxidation potential for (TTMPP)$Fe^{III}Cl$.

In conclusion, with axial hydroxy ligated (*meso*-tetrakis(2,6-disubstituted phenyl)porphinato)iron(III) complexes (i) the first and second 1e oxidation potentials are separated by about 100 mV in dry CH_2Cl_2 and overlap in wet CH_2Cl_2 (this communication and ref 2 and 3) and these pertain to (Porph)$Fe^{III}OH$ → (Porph)$Fe^{IV}O$ → ($^{\bullet+}$Porph)$Fe^{IV}O$ and (ii) a third 1e potential in dry or wet CH_2Cl_2 for ($^{\bullet+}$Porph)$Fe^{IV}O$ → ($^{2+}$Porph)$Fe^{IV}O$ is between 300 and 460 mV more positive (decreasing with electron donation by substituents) than the second oxidation (this study and ref 2, 3, and 6).

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