

of electron transfer, including the existence of "inverted" behavior.²⁴

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Electrochemical Characterization of Six-Coordinate Nitrosyl σ -Bonded Iron-Phenylporphyrins

Sir:

The electrochemistry of five-coordinate nitrosyl iron porphyrins has been well documented in the literature.¹⁻³ The air-stable species contain Fe(II), which (depending on the solvent donor properties and porphyrin ring) is oxidized to Fe(III) in a range of potential between 0.60 and 0.80 V vs. SCE. For the specific case of (TPP)Fe(NO) (TPP = tetraphenylporphyrin), oxidation of Fe(II) to Fe(III) occurs at 0.75 V.² In contrast, σ -bonded alkyl or aryl iron porphyrins contain Fe(III) in the air-stable form. These complexes may be reduced to Fe(II) in the range of -0.70 to -1.00 V, depending on the porphyrin ring basicity, the type of bound alkyl or aryl group, and the solvent donor properties.⁴⁻⁸ For the specific case of (TPP)Fe(C₆H₅) in PhCN, reduction to Fe(II) occurs at -0.70 V.⁸

The above two types of complexes represent opposite extremes in synthetic iron porphyrin electrochemical reactivity. The Fe(III)/Fe(II) potential for (TPP)Fe(NO) is the most positive ever measured for a five-coordinate iron tetraphenylporphyrin and indicates extreme stability of the Fe(II) oxidation state. In contrast, the Fe(III)/Fe(II) reaction of (TPP)Fe(C₆H₅) is one of the most negative ever measured for a five-coordinate iron tetraphenylporphyrin and indicates extreme stability of the Fe(III) oxidation state toward reduction.

In an attempt to better understand the opposite stabilizing effects of the nitrosyl and alkyl groups, we have investigated the electrochemistry of six-coordinate (P)Fe(C₆H₅)(NO) (where P = OEP (octaethylporphyrin) or TPP). These complexes may be obtained by exposure of (P)Fe(C₆H₅) to NO gas either in solution or as a solid powder. The six-coordinate complexes have a slightly bent Fe-N-O bond, as characterized by the 1790-cm⁻¹ IR NO stretching frequency.⁹ Their UV-visible and ¹H NMR spectra have been discussed and the complexes tentatively characterized as low-spin Fe(II) species.⁹ The electrochemical oxidation and reduction of (P)Fe(C₆-

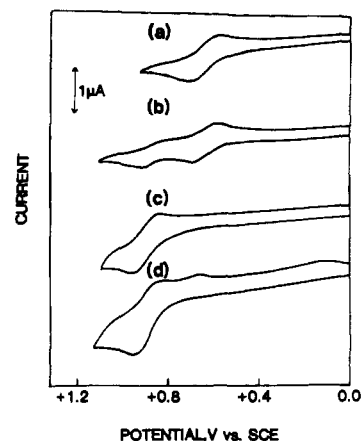


Figure 1. Cyclic voltammograms of 1.09×10^{-3} M (TPP)Fe(C₆H₅) and (TPP)Fe(C₆H₅)(NO) in PhCN with 0.1 M TBA(PF₆) (scan rate 0.10 V/s). Total NO pressure: (a) 0 mm; (b) 29 mm; (c) 72 mm; (d) 171 mm.

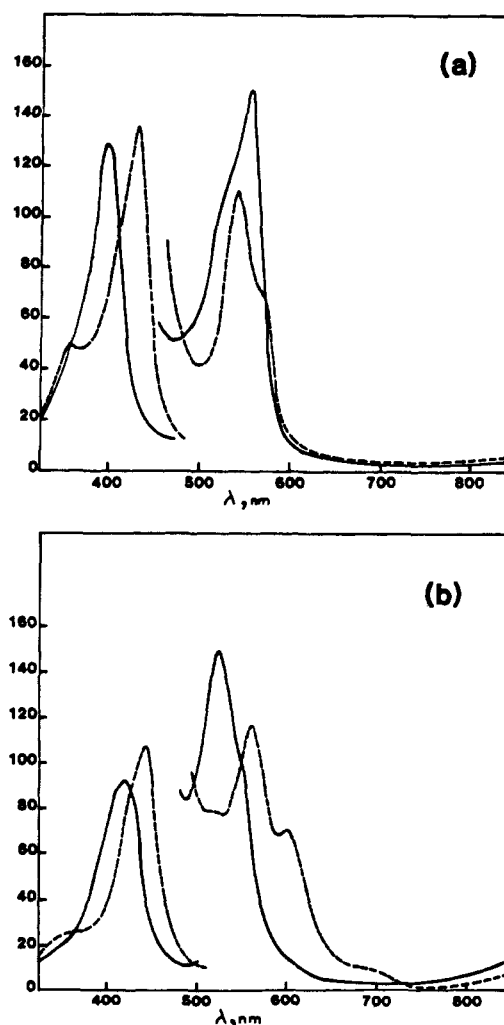


Figure 2. Electronic absorption spectra of (a) 4.96×10^{-5} M (TPP)Fe(C₆H₅) in the presence of 7 mm NO and (b) 2.80×10^{-5} M (OEP)Fe(C₆H₅) in the presence of 8 mm NO, both in PhCN with 0.1 M TBA(PF₆). (P)Fe(C₆H₅) is represented by the solid lines and (P)Fe(C₆H₅)(NO) by the dotted lines.

H₅)(NO) were carried out at a Pt electrode in PhCN (benzotrionitrile) under various NO pressures.

As seen in Figure 1a, the electrochemical oxidation of (TPP)Fe(C₆H₅) in PhCN occurs at 0.61 V in the absence of NO gas. Both the shape of the peaks and the current dependence on scan rate suggest a diffusion-controlled one-

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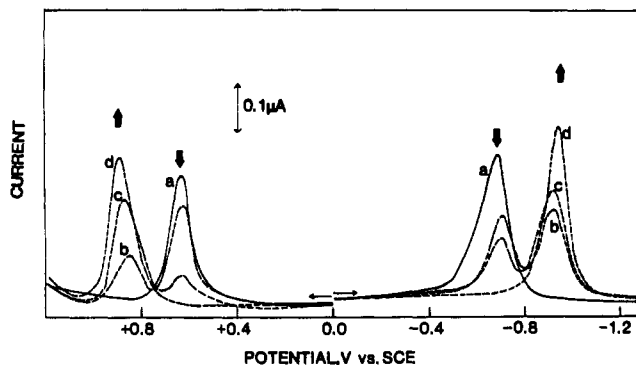
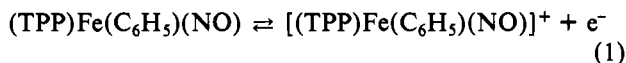


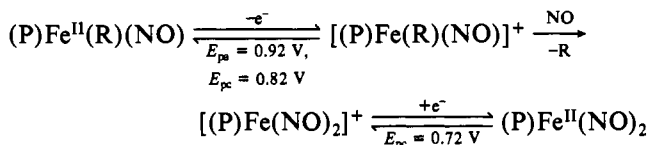
Figure 3. Differential pulse polarograms of 1.09×10^{-3} M (TPP)- $\text{Fe}(\text{C}_6\text{H}_5)$ and (TPP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ in PhCN with 0.1 M TBA(PF_6) (scan rate 0.005 V/s, modulation amplitude 25 mV). Total NO pressure: (a) 0 mm; (b) 29 mm; (c) 48 mm; (d) 72 mm.

electron transfer. This wave was still present (but in reduced currents) under an NO pressure of 29 mm (Figure 1b). The currents for this process further decreased with increase of NO pressure, and the wave totally disappeared under an NO pressure of 72 mm (Figure 1c), where a new reversible process was present (at $E_{1/2} = 0.86$ V). At this point, the spectrum of the solution was monitored and indicated complete conversion of (TPP) $\text{Fe}(\text{C}_6\text{H}_5)$ to (TPP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$. The spectrum of this latter species is given in Figure 2a and agrees with similar spectra in the literature.⁹ Thus, the electrode reaction at 0.86 V can be written as



The oxidation-reduction of (TPP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ is less reversible at high NO pressures, and some decomposition of the oxidation product occurs. The initial (TPP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ is still oxidized to $[(\text{TPP})\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})]^+$ at $E_{1/2} = 0.86$ V, but this species rapidly reacts with excess NO to yield a mixture of $[(\text{TPP})\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})]^+$ and $[(\text{TPP})\text{Fe}(\text{NO})_2]^+$ in solution. Both singly oxidized species are then reduced on the reverse potential sweep, giving cathodic peaks at $E_{pc} = 0.82$ and 0.72 V,¹⁰ respectively. This is illustrated in Figure 1d (for oxidation under 171 mm NO pressure), and the overall oxidation-reduction mechanism at high NO concentrations is shown in Scheme I.

Scheme I



Addition of NO to (TPP) $\text{Fe}(\text{C}_6\text{H}_5)$ and (TPP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ was also monitored by differential pulse polarography. This technique was previously used² to identify (TPP) $\text{Fe}(\text{NO})_2$ and is useful to differentiate reduction waves due to the porphyrin moiety from the reduction of free NO, which yields significant currents at NO pressures higher than 100 mm. This is shown in Figure 3, which records differential pulse polarograms of (TPP) $\text{Fe}(\text{C}_6\text{H}_5)$ as a function of NO pressure. As seen in this figure, quantitative conversion of (TPP) $\text{Fe}(\text{C}_6\text{H}_5)$ to (TPP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ occurs at an NO pressure of 72 mm. This latter compound is reduced at -0.92 V. No evidence of intermediates was found under our experimental conditions, although at higher concentrations of NO, bis-

(nitrosyl) adducts were present.

Similar electrochemistry was also observed for addition of NO to (OEP) $\text{Fe}(\text{C}_6\text{H}_5)$ although, in this case, conversion to (OEP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ required greater than 200 mm NO pressure. Formation of (OEP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ was ascertained under electrochemical conditions by comparing the UV-visible spectrum of the solution with that already reported.^{9,11} The six-coordinate (OEP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ is oxidized at 0.73 V and reduced at -1.16 V. The shapes of the cyclic voltammograms and differential pulse polarograms indicate a reversible oxidation to yield $[(\text{OEP})\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})]^+$ and a quasi-reversible reduction to yield $[(\text{OEP})\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})]^-$.

It is significant to note that the reversible oxidations of (TPP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ and (OEP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ involve neutral compounds formally characterized as Fe(II). Thus, it appears that the effect of an NO molecule in stabilizing the iron(II) porphyrin oxidation state is greater than that of the σ -bonded phenyl group, which produces Fe(III) species. Finally, potentials for oxidation and reduction of (P) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ and (P) $\text{Fe}(\text{NO})$ are separated by only 40–110 mV, again indicating the strong effect of the NO group in determining oxidation-reduction potentials.

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- (11) (OEP) $\text{Fe}(\text{C}_6\text{H}_5)$ (1.31×10^{-3}) reacted under 180 mm NO gas to yield the new (OEP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ species, which had the following absorbance maxima (λ , nm ($10^{-3}\epsilon$)): 360 (50), 430 (140), 550 (27), 575 (sh). (TPP) $\text{Fe}(\text{C}_6\text{H}_5)$ (1.09×10^{-3} M) reacted under 72 mm NO gas to yield (TPP) $\text{Fe}(\text{C}_6\text{H}_5)(\text{NO})$ (λ , nm ($10^{-3}\epsilon$)): 370 (sh), 445 (16), 515 (sh), 560 (27), 600 (sh), 690 (sh).

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Electrochemical Generation of New Dinuclear Ruthenium Acetamidate Complexes

Sir:

Recently we reported the synthesis and electrochemical properties of a new class of diruthenium(II,III) dimers.¹ The initial reported compound, $\text{Ru}_2(\text{HNOCCF}_3)_4\text{Cl}$, has the same cage structure as that of the *N*-phenylacetamidato-bridged dirhodium(II,II) dimer² $\text{Rh}_2(\text{PhNOCCH}_3)_4$ but differs from the well-studied dirhodium^{3,4} and diruthenium⁵ carboxylates in that the bridging ligands contain mixed oxygen and nitrogen donor atoms rather than all oxygen donor groups.

The electrochemistry of $\text{Ru}_2(\text{HNOCCF}_3)_4\text{Cl}$ has been carried out in several solvents with, and without, excess chloride ions as supporting electrolyte¹ and is quite similar to that

(10) (TPP) $\text{Fe}(\text{NO})_2$ and (TPP) $\text{Fe}(\text{NO})$ are oxidized at the same potential (see ref 2). However, under >170 mm NO gas, the predominant species was found to be the bis(nitrosyl) complex.

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