separated by fractional condensation, measured, and identified by infrared spectroscopy. It consisted of FNO_2 (2.09 mmol), CO_2 (2.1 mmol), and COF_2 (0.2 mmol). The white solid residue (91 mg, weight calculated for 2.10 mmol of LiF and 0.25 mmol of CsF 92.5 mg) consisted of LiF and CsF.

Synthesis of $FClO_2$. The reaction was carried out as described above for $LiNO_3$ and COF_2, with use of $NaClO_3$ (1.41 mmol), COF_2 (2.00 mmol), and CsF (0.3 mmol) at 85 °C for 46 h. The products consisted of $FClO_2$ (0.62 mmol, 44% of theory), CO_2 (0.64 mmol), unreacted COF_2, and smaller amounts of Cl_2 and material noncondensable at −196 °C.

Acknowledgment. We are grateful to R. D. Wilson for help with some of the experiments and to the U.S. Army Research Office for financial support of this work.

Registry No. COF_2, 353-50-4; CsF, 13400-13-0; FNO_2, 10022-50-1; $LiNO_3$, 7790-69-4; $FClO_2$, 13637-83-7; $NaClO_3$, 7775-09-9; $NaNO_3$, 7631-99-4; $CsNO_3$, 7789-18-6; $LiClO_4$, 7791-03-9.

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Electrocatalytic Reduction of Nitrite Using Simple Coordination Complexes of Iron and Ruthenium

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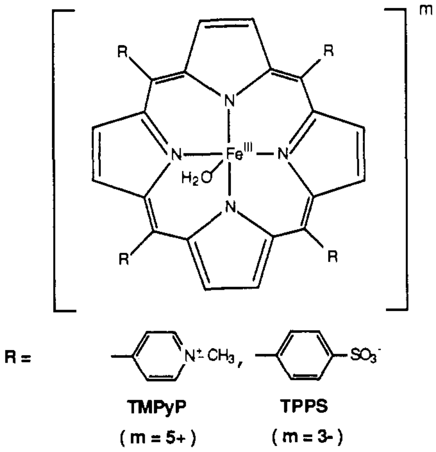
The reduction of nitrite to ammonia is an important metabolic reaction that is catalyzed by the nitrite reductase enzymes.[1] The reduction is a complex multielectron process

$$NO_2^- + 7H^+ + 6e^- \rightarrow NH_3 + 2H_2O \qquad (1)$$

which, by inference, presents formidable mechanistic demands. Given the implied mechanistic complexity, it might have been expected that the facile reduction of NO_2^- would be restricted to enzymatic systems and not be a property shared by simple coordination complexes. However, we showed earlier that the water-soluble iron porphines $[Fe(TPPS)(H_2O)_n]^{3-}$ and $[Fe(TMPyP)(H_2O)_n]^{5+}$ (TPPS = *meso*-tetrakis(*p*-sulfonatophenyl)porphine, TMPyP = *meso*-tetrakis(1-methyl-4-pyridiniumyl)porphine) are effective electrocatalysts for this reduction.[2,3]



Mechanistic studies have shown that the initial stages in the catalyzed reactions involve reduction of nitrite bound to Fe(II) as NO^+. The stoichiometric reduction of nitrite bound as NO^+ has also been shown to occur in polypyridyl complexes of ruthenium and osmium. Mechanistic studies based on these complexes have helped to elucidate the steps involved in the overall reductions,[4,5] steps that may occur in the enzymatic reactions as well.

Table I. Current Efficiencies for Controlled-Potential Electrolyses[a]

catalyst	pH	E_{app}, V[b]	current efficiency, %[c]			
			N_2O	N_2	NH_3OH^+	NH_4^+
$[Ru^{II}(Hedta)(NO^+)]$	5.0	−0.75	16 ± 1	14 ± 2	20 ± 6	54 ± 5
$[Fe^{II}(Hedta)(NO^\bullet)]^-$ [d]	5.0	−0.90	22	13	30	31
$[Fe(H_2O)_6]^{2+}$	2.1	−0.70	74	9	0	23

[a] At room temperature with $[NO_2^-]$ = 10 mM and [catalyst] = 0.1 mM except where noted. The working electrode was a Hg pool with an area of 12.6 cm^2. In all cases the electrolyses were taken to completion. [b] The potential applied. [c] The current efficiency percentage for each of the products was calculated from the following formula: current efficiency (%) = $100(m_i n_i \mathfrak{F})Q_f$. m_i is moles of product formed, n_i is the n value for its formation ($n = 4$ for N_2O, $n = 6$ for N_2, $n = 4$ for NH_3OH^+, and $n = 6$ for NH_4^+), $\mathfrak{F}$ is the Faraday constant, and Q_f is the total charge passed during the electrolysis. Hydrazine was not observed in any experiment within the limit of our detection (<10% current efficiency). Typical uncertainties are given for the first electrolysis. [d] 0.5 mM.

Both the electrocatalysts and the enzymes have as their active sites the iron heme group. Given the "magic" of iron heme sites in biological systems, where they play a role in such diverse processes as oxygen transport, catalytic oxidations, and electron transfer, the question arises as to whether the catalytic reduction of nitrite is a property unique to the porphyrin ligand environment. We demonstrate here that the essential features of nitrite reduction are maintained in simple coordination complexes, that the key is the metal–NO interaction, and that, as shown earlier for the reduction of NO,[6,7] the electrocatalysis is a general phenomenon.

Experimental Section

Chemicals. $FeSO_4 \cdot 7H_2O$, $Na_2H_2edta \cdot 2H_2O$, phthalic acid, tetraethylammonium hydroxide, and hexafluorophosphoric acid (60 wt %) were purchased from Aldrich Chemical Co. KH_2PO_4, Na_2SO_4, and concentrated H_3PO_4 were obtained from Fisher Scientific. All chemicals were used without further purification. $[Ru^{III}(Hedta)(H_2O)]$ and $[Fe^{II}(Hedta)(H_2O)]^-$ were prepared by using methods previously published.[8,9] $[Fe^{II}(Hedta)(NO^\bullet)]^-$ was generated by the in situ reaction between $Fe^{II}SO_4 \cdot 7H_2O$, $Na_2H_2edta \cdot 2H_2O$, and NO gas as described earlier.[7,10] $[Ru^{II}(Hedta)NO]$ was isolated after the direct reaction between $[Ru^{III}(Hedta)(H_2O)]$ and NO gas.[11]

Electrochemical Apparatus. Differential pulse voltammetric experiments were performed on a PAR 174 apparatus, while cyclic voltammetry and bulk electrolyses utilized a PAR 173 potentiostat coupled with a PAR 179 digital readout and an in-house-designed super cycle. Simple one-compartment cells consisting of an SSCE reference electrode and a platinum auxiliary electrode were used for routine cyclic voltammetry and differential pulse experiments. The cell used for bulk electrolyses was a two-compartment gastight cell in which there was a porous Vycor divider between the Pt auxiliary electrode and the working electrode. The working electrode was a Hg pool. The cell design allowed for a gas inlet and outlet, a separate working electrode for obtaining cyclic voltammograms during electrolyses, and a manometer, which was used for

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equalization of internal and external pressures during gas sampling in the nitrite reductions. Buffer solutions were prepared from mixtures of H_3PO_4 or phthalic acid with $[NEt_4](OH)$.

Methods of Analysis for NH_2OH and NH_3. Analyses for NH_2OH and NH_3 as NH_3OH^+ and NH_4^+ were accomplished by using a Dionex Model 2000i ion chromatograph equipped with an HPIC-CS2 column. The eluent was a mixture of 30 mM H_3PO_4 and 30 μM Cu_2SO_4 in H_2O. It was necessary that both the concentration of $[NEt_4]^+$ be lowered and the pH of the sample be adjusted to 2 prior to analsis. This was accomplished by partial precipitation of the $[NEt_4]^+$ ion by the addition of concentrated HPF_6 until the sample pH was approximately 2.

Methods of Analysis for N_2O and N_2. Gas analyses were performed by GC by using a Hewlett-Packard Model 5890A gas chromatograph equipped with a thermal conductivity detector and a strip-chart recorder. N_2O analyses were performed on a Porapak Q column at room temperature, while N_2 analyses were performed on a 5A molecular sieve column (both from Alltech Associates) at room temperature. N_2 analyses were performed both before and after electrolysis in order to account for residual atmospheric N_2 in the cell before the experiment. Cell leakage was tested and found to be minimal over the time scale of these experiments.

Results and Discussion

Both the complexes $[M^{II}(Hedta)(H_2O)]^-$ (M = Ru, Fe; H_4edta = ethylenediaminetetraacetic acid) and the simple aqua ion $[Fe(H_2O)_6]^{2+}$ exhibit catalytic reactivity toward nitrite reduction. This can be demonstrated by a combination of cyclic voltammetry and controlled-potential electrolysis experiments. For the edta aqua complexes cyclic voltammetric waves are observed at $E_{1/2}$ = −110 mV (M = Fe, pH = 4.65) and at −250 mV (M = Ru, pH = 5.5) vs SSCE. They arise from the aqua-based $M^{III/II}$ couples. In the presence of added nitrite these waves are replaced by new reductive waves, which result from the formation of the corresponding nitrosyl complexes. For the edta complexes, the nitrosyl species responsible for these waves can be prepared by independent synthesis and have been shown to be $[Ru^{II}(Hedta)(NO^+)]$ and $[Fe^{II}(Hedta)(NO^\bullet)]^-$.[11] Typical cyclic voltammograms of these nitrosyls are shown in Figure 1a,b. Chemically reversible reductions are observed at $E_{1/2}$ = −150 and −360 mV vs SSCE for $[Fe^{II}(Hedta)(NO^\bullet)]^-$ and $[Ru^{II}(Hedta)(NO^+)]$ at pH = 4.7 and 4.9, respectively. The reversible waves are followed by chemically irreversible waves at E_p = −850 mV (M = Fe) and −750 mV (M = Ru) at pH = 4.7 and 4.9. These are the same waves that are observed when NO_2^- is added to acidic solutions containing the aquo complexes. The nitrosyl complexes can form either following reduction to M(II) via eq 2 or via the disproportionation in eq 3. Figure 1c shows a cyclic voltammogram

$$[M^{II}(Hedta)(H_2O)]^- + 2H^+ + NO_2^- \rightarrow [M^{II}(Hedta)(NO^+)] + H_2O \quad (2)$$

$$3[Ru^{III}(Hedta)(H_2O)] + NO_2^- \rightarrow [(Hedta)Ru^{III}ORu^{IV}(Hedta)]^- + 3H_2O + [Ru^{II}(Hedta)(NO^+)] \quad (3)$$

of a 1:1 mixture of $[Fe(H_2O)_6]^{2+}$ and NO_2^- at pH = 4.5, which shows the appearance of a new, irreversible reduction at −700 mV vs SSCE.

The pattern of reductions that appear for the edta nitrosyl complexes is reminiscent of the pattern found earlier for the water-soluble iron porphines.[2,3] The waves arise from a series of successive reductions at the bound nitrosyl ligand, e.g., $M(NO^+) + e^- \rightarrow M(NO^\bullet)$. Cyclic voltammograms of acidic solutions containing both $Fe(H_2O)_6^{2+}$ and NO_2^- give less well-defined electrochemistry, but a new reductive wave does appear in the presence of added nitrite as shown in Figure 1c.

The nitrogen-based products obtained by controlled-potential electrolyses of the aqua complexes in the presence of nitrite in acidic solution are shown in Table I. After the addition of excess nitrite and reduction of M(III) to M(II), the dominant forms in solution are the nitrosyl complexes. After complete electrolysis of available nitrite, the aqua complexes reappear in the solution. The applied potentials are only slightly more negative than the potential of the NADPH/NADP couple (E^0 = −560 mV vs SSCE). NADPH is a common source of reducing equivalents for nitrite reduction in the enzymatically catalyzed reactions.

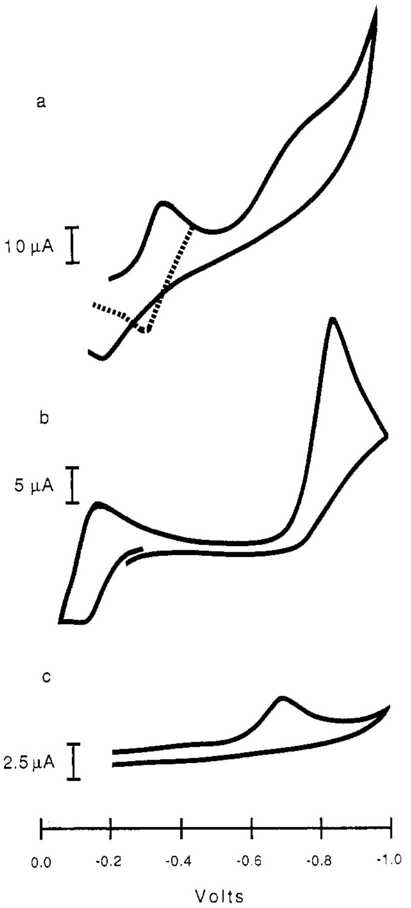

Figure 1. Cyclic voltammograms obtained at a Hg-drop electrode (3–4 μL) at a scan rate of 100 mV/s vs SSCE: (a) [Ru(Hedta)(NO)] at pH 4.9; (b) $[Fe(Hedta)(NO^\bullet)]^-$ at pH 4.7; (c) $[Fe(H_2O)_6]^{2+}$ (as $FeSO_4\cdot7H_2O$) and NO_2^- both at 1 mM at pH 4.5. The concentrations of complexes are 1 mM, and the supporting electrolyte is 0.1 M KH_2PO_4 with the pH adjusted with 0.5 M NaOH in all cases.

The appearance of a range of reduced N-based products is a property that the simple coordination complexes share with the water-soluble iron porphines as electrocatalysts.[2,3] Although direct rate comparisons are difficult to make because of the dependence of the reactions upon pH, potential, and concentration, some qualitative observations based on the magnitudes of limiting currents obtained during the controlled-potential electrolysis experiments can be made. These experiments were carried out at a 12.6-cm² Hg-pool electrode at pH = 4.5–5.0, $[NO_2^-]$ = 10 mM, and [catalyst] = ~0.1 mM. The applied potential, E_{app}, was held at the peak potential for the second reduction, which is irreversible. As for the porphyrins, the active form of the catalyst is the corresponding nitrosyl, which forms rapidly under these conditions. It is the reduction of the nitrosyl complexes that leads to the net reduction of nitrite. For $[Fe(H_2O)_6]^{2+}$ as catalyst, E_{app} was the peak potential for the single irreversible reduction wave. Under these conditions, catalytic currents are comparable for $[Ru(Hedta)(H_2O)]^-$ and $[Fe(Hedta)(H_2O)]^-$ but are lower than catalytic currents for $[Fe(TPPS)(H_2O)_n]^{3-}$ by a factor of 40–50. Under the same conditions but at pH = 2.1, the catalytic current for $[Fe(Hedta)(H_2O)]^-$ was greater by approximately 6-fold than for $[Fe(H_2O)_6]^{2+}$.

Our experiments show clearly that the ability to act as aqueous electrocatalysts is a property of simple coordination complexes of Fe and Ru. Mechanistically, the first step involves nitrosyl formation followed by reduction of the nitrosyl. Although there may be rate advantages for the iron porphines, our initial results suggest that the same mechanistic pathways exist and that the key to the underlying chemistry lies largely in the nature of the metal–NO interaction in the initial and intermediate stages of the reaction. Work currently in progress involves an investigation into the factors controlling the relative product yields observed, and that will be the subject of a future paper.

Acknowledgment is made to the National Institutes of Health under Grant No. 5-RO1-GM32296-05 for support of this research.

Registry No. $[Ru^{II}(Hedta)(H_2O)]^-$, 117687-36-2; $[Fe^{II}(Hedta)(H_2O)]^-$, 117687-37-3; $[Fe(H_2O)_6]^{2+}$, 15365-81-8; NO_2^-, 14797-65-0; NH_2OH, 7803-49-8; NH_3, 7664-41-7; N_2O, 10024-97-2; N_2, 7727-37-9; $[Ru^{II}(Hedta)NO]$, 117687-38-4; $[Fe^{II}(Hedta)(NO^{\bullet})]^-$, 117687-39-5; $[Fe(TPPS)(H_2O)]^{3-}$, 53194-20-0.

Additions and Corrections

1988, Volume 27

Robert A. Scott, Cheryl E. Coté, and David M. Dooley*: Copper X-ray Absorption Spectroscopic Studies of the Bovine Plasma Amine Oxidase–Sulfide Complex.

Page 3859. The symbols in the caption to Figure 1 have been reversed. The correct caption should read as follows: Copper K absorption edge (a) and EXAFS (b) spectra for resting (oxidized) bovine plasma amine oxidase (- - -) and its complex with sulfide (—). In the Experimental Section, third sentence, the definition of enzyme activity should read as follows: One enzyme unit catalyzes the oxidation of 1 μmol min^{-1} of benzylamine to benzaldehyde.—David M. Dooley