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Iron Porphyrin-based Electrocatalytic Reduction of Nitrite to Ammonia

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Electrocatalytic reduction of nitrite to ammonia has been demonstrated using a water-soluble iron porphyrin as catalyst.

The stoicheiometric or near-stoicheiometric reduction of co-ordinated nitrite or nitrosyl to ammonia has been observed in complexes of Fe, Ru, and Os[1—3] and a mechanism has been proposed based on a series of one-electron reductions of the corresponding nitrosyl complexes.[3] Recently, catalytic reduction of NO has been reported using certain iron complexes.[4] The naturally occurring enzyme nitrite reductase,[5] which contains an iron isobacteriochlorin,[6] achieves this transformation catalytically, and we find that the water soluble iron porphyrin $Fe^{III}(TPPS)^{3-}.3Na^{+}.12H_2O$[7] [$H_2TPPS^{4-}$ = tetra-anionic form of meso-tetrakis(*p*-sulphonatophenyl)porphine] acts as an effective electrocatalyst for the reduction of nitrite to ammonia.

Using 0.5—1.0 M phosphate buffer, ~ 0.1 M NO_2^- in the pH range 6.5—7.4, electroreduction at −0.9 V (*vs.* saturated calomel electrode) gives NH_3 (by g.c.) with up to 17 turnovers of the porphyrin complex (moles of NH_3 formed/moles of catalyst) with current efficiencies of 46—72%. Under these conditions the current background in the absence of catalyst is negligible. Dinitrogen is also obtained as a minor product but neither NH_2OH nor N_2H_4 was detected. To date, we have been unable to account for the remaining reductive equivalents, but it is interesting that spectral studies show that the catalyst is >85% unchanged after 6—7 turnovers.

The mechanism of reduction has been investigated by cyclic voltammetry and differential pulse polarography using activated and unactivated carbon electrodes.[8] In the absence of nitrite, but with 0.1 M buffer and 0.6 M Na_2SO_4 added, a pH independent (pH < 7) Fe^{III}/Fe^{II} wave appears at $E_{\frac{1}{2}} = -0.23$ V. The added Na_2SO_4 improves the reversibility of the electrode process but promotes formation of the μ-oxo dimer, $[\{Fe^{III}(TPPS)\}_2O]^{8-}$, at pH > 4.0. On addition of nitrite, the corresponding nitrosyl complex appears *via* two pathways. In acidic solutions (pH < 3.0) NO is generated by disproportionation of HONO ($3NO_2^- + 2H^+ \rightarrow NO_3^- + 2NO + H_2O$) and then undergoes a reaction with the Fe^{III} porphyrin to give the nitrosyl complex, $[Fe^{III}(TPPS)(H_2O)]^{3-} + {}^{\bullet}NO \rightarrow [Fe^{II}(TPPS)(NO^+)]^{3-}$. The nitrosyl complex is spectrally similar [$\lambda_{max.}$ (visible region) 536 nm] to that generated when $Fe^{II}(TPP)(NO)$ (TPP^{2-} = dianion of meso-tetraphenylporphine) is oxidized in PhCN at + 0.75 V ($\lambda_{max.}$ = 539 nm).[9] At pH > 3.0 with 10 equiv. of NO_2^-, and no Na_2SO_4, $[Fe^{III}(TPPS)]^{3-}$ is the dominant species in solution, probably as the axially ligated mono- or di-aquo ion. However, electrochemical reduction of Fe^{III} to $[Fe^{II}(TPPS)]^{4-}$ (past −0.23 V) results in the rapid ($t_{\frac{1}{2}}$ < 1 s) appearance of the reduced nitrosyl complex, $[Fe^{II}(TPPS)(NO)]^{4-}$, presumably *via* $[Fe^{II}(TPPS)]^{4-} + NO_2^-$

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$$\text{(pH} > 2.6)\ \text{Fe}^{\text{II}}\text{–NO}^{\bullet} + e^- \rightleftharpoons \text{Fe}^{\text{II}}\text{–NO}^-$$

$$(2.6 > \text{pH} > 2.1)\ \text{Fe}^{\text{II}}\text{–NO}^{\bullet} + e^- + 1\text{H}^+ \rightleftharpoons \text{Fe}^{\text{II}}\text{–NHO}$$

$$(2.1 > \text{pH} > 1.4)\ \text{Fe}^{\text{II}}\text{–NO}^{\bullet} + e^- + 2\text{H}^+ \rightleftharpoons \text{Fe}^{\text{II}}\text{–NH}_2\text{O}\ (\text{or Fe}^{\text{V}}\equiv\text{N})$$

$$(\text{pH} < 1.4)\ \text{Fe}^{\text{II}}\text{–NOH} + e^- + 1\text{H}^+ \rightleftharpoons \text{Fe}^{\text{II}}\text{–NH}_2\text{O}\ (\text{or Fe}^{\text{V}}\equiv\text{N})$$

Scheme 1

$+ 2H^+ + e^- \rightarrow [Fe^{II}(TPPS)(NO)]^{4-} + H_2O$, by analogy with the known acid–base, nitrosyl–nitrite chemistry for polypyridine complexes of Ru[10] and Os[11] and for the nitroprusside ion, $[Fe(CN)_5NO]^{2-}$.[12]

For the nitrosyl complex, a pH independent, somewhat irreversible electrode process is observed at ~ + 0.35 V for the couple, $[Fe^{II}(TPPS)(NO^+)]^{3-} + e^- \rightarrow [Fe^{II}(TPPS)(NO^{\bullet})]^{4-}$. For the TPP complex, the potential for the analogous couple occurs at + 0.75 V in PhCN.[9] A second NO-based reduction is observed in the region −0.4 to −0.7 V for the couple $[Fe^{II}(TPPS)(NO^{\bullet})]^{4-} + e^- \rightarrow [Fe^{II}(TPPS)(NO^-)]^{5-}$ ($E_{\frac{1}{2}} \sim -0.88$ V for the analogous TPP couple in PhCN)[9] which shows a complex dependence on pH in acidic solutions. Using differential pulse techniques, the observed variations in peak potentials (E_p) with pH in the presence of 0.6 M Na_2SO_4 are consistent with the electrode processes in Scheme 1 for the TPPS system. It should be noted that direct evidence for intermediates like M^{II}–NO and M^{II}–NHO has been obtained for polypyridine complexes of Ru and Os.[3b,c]

From pH 4 to 7 the subsequent steps following the second reduction of the bound nitrosyl ($Fe^{II}–NO^{\bullet} \rightarrow Fe^{II}–NO^-$) are relatively slow. At an activated carbon electrode between pH 3.1 and 3.6, a broad, featureless, apparently multi-electron, multi-proton process is observed in the range −0.55 to −1.0 V. Peak currents in this potential region are strongly enhanced in more acidic solution. Reduction into the multi-electron wave apparently leads to the further direct reduction to ammonia, $Fe^{II}–NO^- + 4e^- + 5H^+ \rightarrow Fe^{II}–NH_3 + H_2O$, without the build-up of further intermediates since, in contrast to polypyridine complexes of Ru,[3] reverse scan gives no evidence for additional intermediates. The advantage of the iron porphyrin complex as a catalyst is that once the reduction to NH_3 is complete, substitution at the relatively labile axial position of the porphyrin complex allows for facile incorporation of an additional nitrosyl group thus completing the catalytic cycle. The polypyridine complexes of Ru and Os are substitution inert and the newly formed NH_3 group remains firmly bound.

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