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Electrocatalytic Reduction of ROOH by Iron Porphyrins

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Two-electron reduction of the O−O bond (in H_2O_2, alkyl hydroperoxides, and peroxyacids) is a thermodynamically favorable but kinetically slow process.[1] Heme-catalyzed reduction of this bond is an obligatory step in aerobic metabolism,[2] including energy generation by terminal oxidases, detoxification by catalases, and metabolite transformation by peroxidases and cytochromes P450.[3] Alkylperoxides and peroxyacids are widely used in studies of cytochromes P450 as "shunt" reactants, which upon addition to the oxidized enzyme generate compound I without external reducing equivalents, required in the catalytic cycle with O_2.[4] Electrochemistry has been employed extensively in kinetic studies of O_2 and H_2O_2 catalytic reductions by iron porphyrins in an aqueous medium at biologically relevant pH and electrochemical potential. Other peroxidic oxidants have not been studied electrochemically, despite the unique information that electrochemistry can provide for understanding the mechanism of O−O bond heterolysis at an iron porphyrin site.[4]

Here we report the kinetics and the mechanism of electrocatalytic reduction of common peroxidic oxidants, ^tBuOOH (TBHP), CH_3CO_3H (PAA), m-$ClC_6H_4CO_3H$ (CPBA), and $KHSO_5$,[5] at iron tetraphenylporphyrin and its superstructured derivatives (Figure 1A), and the effect of distal and proximal environments on kinetic parameters.
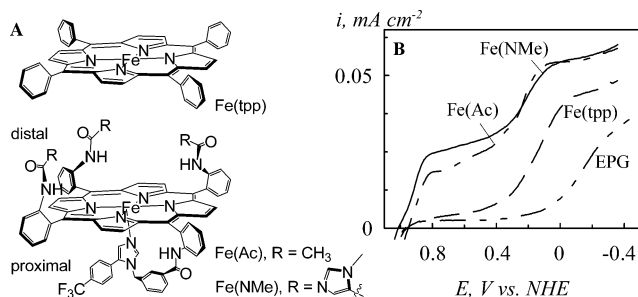
Figure 1. (A) Chemical structures of the studied catalysts. (B) Reduction of 0.125 mM PAA at an EPG electrode modified with Fe(NMe), Fe(Ac), and Fe(tpp) and at bare EPG. $v = 0.02$ V s^{-1}, $\omega = 200$ rpm, $\Gamma = 0.75$ nmol cm^{-2}, 0.1 M KPF$_6$, pH 7.
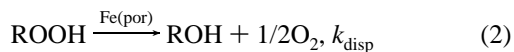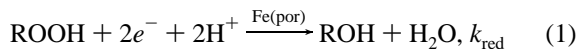
Electrocatalysis was studied by rotating disk and ring-disk voltammetry[6] in buffered aqueous solutions under N_2 with the water-insoluble Fe(por) catalysts immobilized on an edge-plane graphite (EPG) disk electrode.[7] The iron porphyrins significantly decrease the overpotential for ROOH reduction (Figure 1B). Catalytic reduction of TBHP, KHSO$_5$, PAA, and CPBA at **ferric**-Fe(NMe) and Fe(Ac) accounts for catalytic currents at potentials more oxidizing than 0.4 V. An increase in the catalytic current corresponding to faster turnover is observed at more reducing potentials and results from **ferrous**-Fe(NMe) and Fe(Ac) as the

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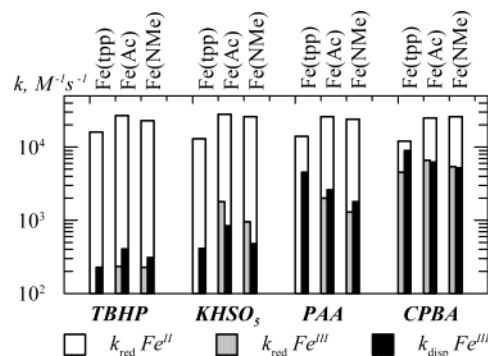
Figure 2. Apparent catalytic rate constants for reactions 1 and 2 at pH 7 and E (V vs NHE) = −0.05 (Fe^{II}(NMe)), −0.1 (Fe^{II}(Ac)), −0.15 (Fe^{II}(tpp)), and 0.7 (Fe^{III}).

catalytically active form. The onsets of these two catalytic waves correlate with the Fe$^{IV/III}$ and Fe$^{III/II}$ potentials in the absence of reactant. A similar behavior is observed for Fe(tpp) with CPBA but not TBHP, KHSO$_5$, or PAA, indicating that axial imidazole ligation to Fe^{III}(por) increases the ferriporphyrin's catalytic activity. In contrast, distal imidazoles do not facilitate the catalysis, as the kinetic parameters for Fe(Ac) and Fe(NMe) catalysis are the same (Figure 2).

The kinetic parameters were derived from Tafel and Koutecky−Levich plots.[7] For ferric-form-catalyzed reductions ($E > 0.4$ V), the slopes of the Koutecky−Levich plots were about twice those theoretically possible, revealing a competition between catalytic electroreduction and disproportionation[8] of the peroxidic reactant:

$$ROOH + 2e^- + 2H^+ \xrightarrow{Fe(por)} ROH + H_2O, k_{red} \quad (1)$$

$$ROOH \xrightarrow{Fe(por)} ROH + 1/2 O_2, k_{disp} \quad (2)$$

This assertion was confirmed by rotating ring-disk voltammetry, where the Au ring electrode was employed to quantify the rate of O_2 production by disproportionation of ROOH. From the disk and ring currents, apparent second-order rate constants, k_{red} and k_{disp} (Figure 2), were estimated:[7]

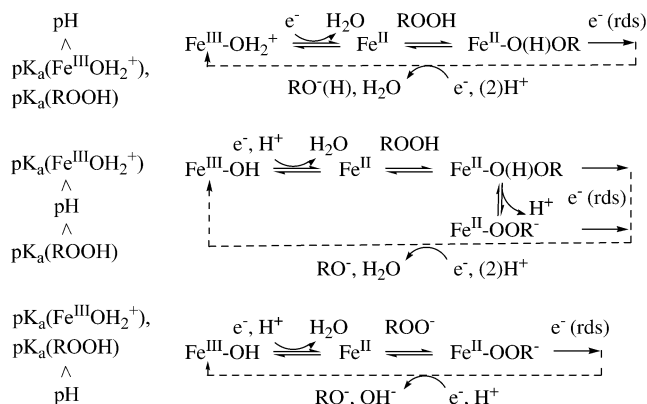$$i_{disk} = nFk_{red}\Gamma c[1 - (i_{disk} + 2i_{ring}/N)/i_{lim}]$$

$$2i_{ring}/N = nFk_{disp}\Gamma c[1 - (i_{disk} + 2i_{ring}/N)/i_{lim}]$$

At pH 7, the slopes of plots of applied potential vs the log of the kinetic current (Tafel plots) were −60 mV/dec[7] at high currents, suggesting catalyst redox preequilibrium followed by a nonredox rate-determining step (rds), e.g., reactant binding or its further deprotonation,[9] as a possible mechanism. The steeper slopes at low currents (−87 to −98 mV/dec) may suggest an electron-transfer rds, with the slopes of <−120 mV/dec arising from competing oxidation of graphite and/or water at most positive potentials.

pH
∧
pK$_a$(Fe^{III}OH$_2$$^+$),   Fe^{III}-OH$_2$$^+$ ⇌ Fe^{II} ⟶ Fe^{II}-O(H)OR ⟶
pK$_a$(ROOH)   e$^-$ H$_2$O ROOH   e$^-$ (rds)
                                       RO$^-$(H), H$_2$O   e$^-$, (2)H$^+$

pK$_a$(Fe^{III}OH$_2$$^+$)   e$^-$, H$^+$ H$_2$O ROOH
∧   Fe^{III}-OH ⇌ Fe^{II} ⟶ Fe^{II}-O(H)OR ⟶
pH   Fe^{II}-OOR$^-$ ⟶ H$^+$ e$^-$ (rds)
pK$_a$(ROOH)
                                    RO$^-$, H$_2$O   e$^-$, (2)H$^+$

pK$_a$(Fe^{III}OH$_2$$^+$),   e$^-$, H$^+$ H$_2$O ROO$^-$ e$^-$ (rds)
pK$_a$(ROOH)   Fe^{III}-OH ⇌ Fe^{II} ⟶ Fe^{II}-OOR$^-$ ⟶
∧
pH   RO$^-$, OH$^-$ e$^-$, H$^+$

Figure 3. Possible mechanism consistent with the kinetic data for reduction of ROOH by ferrous catalysts at different pH. Broken arrows refer to fast steps after rds, which do not contribute to the kinetic law. pK_a(Fe^{III}H$_2$O) = 5.7, 7.7, and 8.4 for Fe(tpp), Fe(Ac), and Fe(NMe);[10] pK_a(ROOH) = 8.2, 9.4, and 16.7 for PAA, KHSO$_5$, and TBHP.

Rapid loss of catalytic activity in alkaline solutions precluded us from obtaining Tafel plots at pH > 7.

The Koutecky−Levich slopes for electrocatalysis by ferrous catalysts correspond to a 2e$^-$ process in accord with the expected reaction (reaction 1). The stoichiometry of the catalysis with respect to the reactant was 1 for all catalyst/reactant combinations, as determined from the slopes of the log i vs log($1 - i/i_{lim}$) plots (i and i_{lim} are the catalytic and diffusion-limited currents, respectively) at different rotation speeds and constant potential.[7] The kinetic currents determined from the Koutecky−Levich plots were proportional to the amount of deposited catalyst up to the coverage of ~0.5 nmol cm^{-2}. Depositing more catalyst did not increase significantly the kinetic currents, in contrast to the reduction of O$_2$ and H$_2$O$_2$, where much thicker films are catalytically active.[10] This difference suggests that steric factors may be important in governing the kinetics of reactant transport within the film.

Under experimental conditions corresponding to the first-order kinetics in both the reactant and the catalyst, the rate law is $i_{kin} = 2Fk_{red}\Gamma c_{ROOH}$, and the apparent second-order rate constants, k_{red}, at a given pH and potential are estimated from the intercepts of the Koutecky−Levich plots (Figure 2). The rates of ROOH reduction at **ferrous** catalysts are independent of the nature of ROOH, suggesting a change in the rate-determining step compared to that in catalysis by the **ferric** form where the rate of catalytic turnover correlates with the redox potential of the reactants.[11]

In the systems with no (or low) Fe^{III} activity (Fe(tpp)/TBHP, PAA, KHSO$_5$; Fe(Ac)/TBHP; Fe(NMe)/TBHP), the Tafel slopes are essentially independent of pH over the pH range 4−12 and close to −120 mV/dec, which is the slope for a slow transfer of the first electron[9] (Figure 3). The systems showing Fe^{III} catalysis were not analyzed due to overlapping of the studied process with residual catalysis by the ferric form.

The pH dependence of potential at constant current derived from Tafel plots indicates three distinct catalytic regimes with slopes of 0, −60, and −120 mV/pH (Figure 4), giving the chemical order in protons, $p = (\partial E/\partial pH)/(\partial E/\partial \log i_{kin})$, of 0, 0.5, and 1. The pH dependence arises from the complex acid−base equilibria of the catalysts and reactants (Figure 3). In an acidic medium, where the dominant acid−base forms of the catalyst and reactant are (por)-FeOH$_2$$^+$ and ROOH, the catalytic currents are independent of pH, and the simplest mechanism involves reduction of (por)Fe^{III}OH$_2$$^+$ to the ferrous form, followed by coordination of ROOH and rate-determining reductive O−O bond cleavage. When both the catalyst
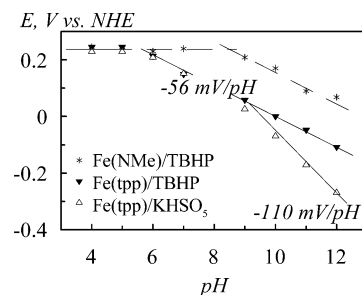
Figure 4. Effect of pH on the electrochemical potential required to achieve a specific turnover rate (i_{kin} = 32 μA cm^{-2}).

and the reactant are deprotonated, the pH dependence is consistent with one acid−base equilibrium, which is likely proton-coupled reduction of (por)Fe^{III}OH to its ferrous form. In the intermediate pH range, where the ferric catalyst is deprotonated but the ROOH is not, a fractional order in protons is observed, suggesting a slow step of deprotonation of the bound reactant preceding (or competing with) the rds.

Catalytic reduction of KHSO$_5$, PAA, and CPBA at ferric-Fe-(NMe) and Fe(Ac) is substantially faster than reduction of H$_2$O$_2$,[10] which is comparable to that of TBHP. This may be related to both the better ligating power of ROOH and more facile O−O bond heterolysis. As we have observed in catalytic reductions of H$_2$O$_2$,[10] ClO$_2$$^-$, BrO$_3$$^-$, and IO$_4$$^-$,[12] an axial imidazole ligation of iron is essential for the biologically relevant catalytic activity of ferric porphyrins. In contrast, the effect of the distal organic moieties is more limited. We expect that the presence of a distal metal (Cu^{II}, Fe^{II}, and Pd^{II}) will enhance the ferrous porphyrins catalysis.

Supporting Information Available: Experimental details and additional electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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