Electrochemical Metalloporphyrin-Catalyzed Reduction of Chlorite

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Multielectron reductions of small inorganic molecules are extraordinarily important in the biosphere. For example, these processes form the basis for both aerobic[1] and most forms of anaerobic (e.g., SO_4^{2-}, NO_3^-, ClO_x^-)[2,3] respiration. These molecules are thermodynamically powerful but inert oxidants, largely because of the unfavorable initial one-electron-transfer step. There are similarities between O_2 and ClO_2^- as oxidants. First, four-electron, four-proton ($4e/4H^+$) reduction of either species is highly exergonic ($\sim$1.2 and $\sim$0.8 V for ClO_2^- and O_2, respectively[4]) but sluggish without catalysis. Second, partial ($2e/2H^+$) reduction generates even stronger oxidants (HClO and H_2O_2, both $\sim$1.3 V[4]). Yet, while catalytic reduction of O_2 has been extensively studied, little is known about molecular catalysis with ClO_2^- as a terminal oxidant.[5,6] Peroxidase and chloroperoxidases can utilize ClO_2^- as a chlorinating agent.[7,8] Synthetic metalloporphyrin-mediated oxygenation[9] or chlorination[10] of organics with ClO_2^- has been reported. Heme-catalyzed dismutation of chlorite to Cl^- and O_2 is carried out by several bacteria[11] and has been utilized for anoxic hydrocarbon bioremediation.[12] A reaction between ClO_2^- and the heme of hemoglobin is thought to initiate the immunoregulatory effect of a chlorite-based drug.[13]

We have investigated a series of metalloporphyrins (Chart 1) as catalysts for the electrochemical reduction of ClO_2^- under anaerobic conditions.[14] The reactivity of these complexes toward O_2 ranges from efficient 4e catalysis (e.g., ImFeIm₃),[16] to 2e reduction of O_2 to H_2O_2 [e.g., Co(tpp)], to the absence of any catalytic activity [Al-(tpp) and Mn(tpp)]. Different distal and proximal environments of these complexes allow probing of the structural requirements for efficient catalytic reduction of ClO_2^-. Electrocatalysis was studied by rotating disk-electrode voltammetry;[15] the water-insoluble complexes were deposited on a graphite electrode in contact with an aqueous electrolyte buffered at pH 7. No reduction of ClO_2^- is observed on unmodified graphite within the stability window of H_2O.

With the exception of Co(tpp) and Al(tpp), which are inert toward ClO_2^-, all other metalloporphyrins catalyze clean 4e reduction. The onset potential of the catalysis indicates that M^{II} is the catalytically active redox state, although low-turnover-frequency (TOF) ClO_2^- reduction by imidazole-ligated *ferric* porphyrins starts at $\sim$0.8 V.[4] A total of 300−400 ClO_2^- molecules are reduced per molecule of Fe catalyst before loss of the activity, whereas Mn and Co porphyrins are inactivated after 20−50 turnovers.

Cl^{II}/Cl^I scavengers (phenol, Cl^-, and 1-amino-1-cyclopropane-carboxylic acid)[6,13] do not affect the apparent redox stoichiometry of the catalysis, but at high concentrations phenol increases the stability of the Fe catalysts.[17] This suggests that catalyst degradation may be mediated in part by free Cl^{II}/Cl^I species, which are either generated in minor side reactions or are intermediates that are

rapidly reduced further. The latter assertion is consistent with the observation that reduction of ClO^- is diffusion-limited throughout the potential range where catalysis is observed. Because none of the metalloporphyrins catalyzes reduction of ClO_x^- ($x = 3, 4$), the 4e redox stoichiometry indicates that chlorite disproportionation, which commonly accompanies reactions of transition metals with ClO_2^-,[6] is not significant in our system.
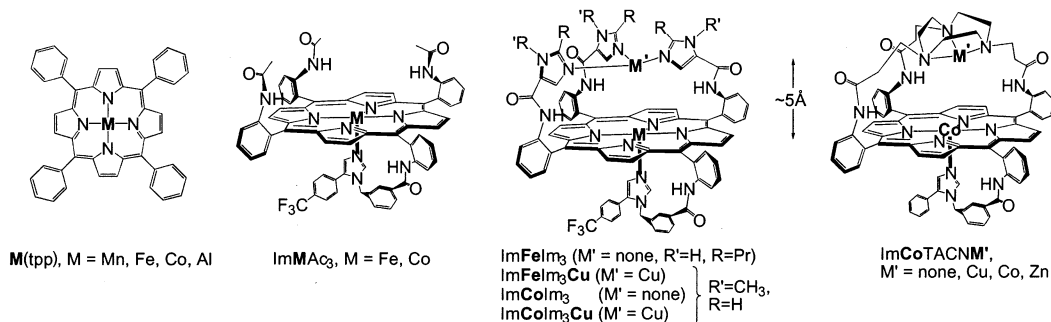
The catalytic rate is first-order both in ClO_2^- and, at catalyst surface coverages below 0.2−2 nmol/cm² (depending on metalloporphyrin), in the catalyst. The apparent second-order rate constants (Figure 1) were measured in the regimes where the TOF is potential-dependent (at 0.2 V)[4] and potential-independent (at −0.25 V). The TOF at 0.2 V reflects the efficiency of the catalysts in mediating electron-transfer (ET) step(s), whereas the TOF at −250 mV is determined solely by the rate(s) of non-ET step(s) (e.g., substrate binding and/or product dissociation). The maximum rate constants of the catalytic ClO_2^- reduction by Fe porphyrins are 2−100 times those reported in the literature for oxidation of simple ferrous salts by ClO_2^-.[6] The kinetics of oxidation of Mn^{II} or Co^{II} by ClO_2^- has not been previously studied.

The activity and stability of the catalysts studied are comparable in reduction of both ClO_2^- and H_2O_2 (Figure 1), including a high-potential onset of low-TOF reduction by imidazole-ligated *ferric* porphyrins. These data are consistent with reduction of ClO_2^- and H_2O_2 proceeding via a similar route, i.e., an oxygen-atom transfer with formation of oxoferryl species ($E(Fe^{IV}/Fe^{III})_{pH\ 7} \approx 0.9$ V).[16a]

In addition to ClO_x^- ($x = 3, 4$), the metalloporphyrins do not react with IO_3^-, but catalytic $6e/6H^+$ reduction of BrO_3^- is observed. The poor ligating properties of ClO_x^- and the lower oxidizing potential of IO_3^- may account for the inertness of these oxoanions. Relative to ClO_2^- or H_2O_2 as substrates, lower TOFs (Figure 1) but greater catalyst stabilities are observed in reduction of BrO_3^-. Fe(tpp) is an exception, being equally effective in catalyzing the reduction of ClO_2^-, H_2O_2, BrO_3^-, and is particularly robust in the latter reaction, retaining its activity for $>6 \times 10^5$ turnovers.

The data in Figure 1 allow some conclusions to be made regarding the effect of the metal and the proximal and distal environments on the efficiency of ClO_2^- reduction. Although $M^{III/II}$ potentials are comparable for imidazole-ligated Fe and Co, ClO_2^- reduction by Fe^{II} porphyrins is >100 times faster than that by Co (or Mn) analogues. This relative reactivity correlates qualitatively with the $M^{IV/II}$ ($M^{II}(por)/M^{III}(por^+)$) potentials. The inertness of Co-(tpp) suggests that the imidazole ligation is important for the catalytic activity of Co porphyrins. In addition, imidazole-ligated Fe centers manifest notably higher TOFs at lower overpotentials. The higher reactivity of imidazole-ligated centers toward O−O bond reduction is usually ascribed to electron donation from the imidazole to the O−O bond;[18] a similar phenomenon may be operative in reduction of ClO_2^-. The effect of the distal environment is more

Chart 1. Chemical Formulas and Abbreviated Names of the Metalloporphyrins Used in This Study[a]

M(tpp), M = Mn, Fe, Co, Al   **ImMAc₃**, M = Fe, Co

ImFeIm₃ (M' = none, R'=H, R=Pr)
ImFeIm₃Cu (M' = Cu)
ImCoIm₃ (M' = none)   R'=CH₃,
ImCoIm₃Cu (M' = Cu)   R=H

ImCoTACNM',
M' = none, Cu, Co, Zn

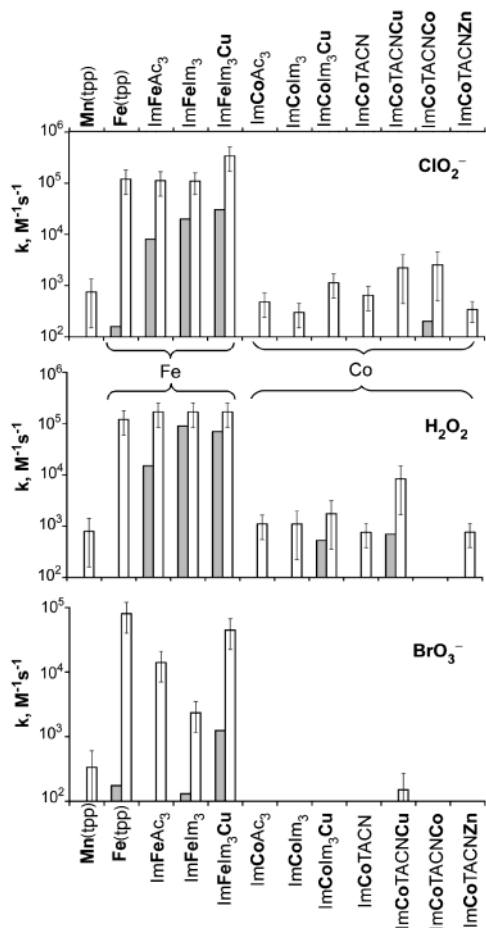[a] The metal−metal separation in bimetallic catalysts is ∼5 Å.[16b]

Figure 1. Apparent second-order catalytic rate constants, k, for electrochemical reduction of ClO_2^-, H_2O_2, and BrO_3^- in aqueous electrolytes at pH 7. Shaded rectangles: rate constants at 200 (ClO_2^-, H_2O_2) or 150 mV (BrO_3^-). Open rectangles: values at −250 mV. Rate constants <100 M^{-1} s^{-1} could not be measured with sufficient precision and are not listed.

limited, except in slower reduction of BrO_3^-, where a redox-active distal metal accelerates the catalysis (e.g., the TOF of the FeCu catalyst is >20 times that of the Fe-only analogue, and a CoCu derivative is the only catalytically active Co porphyrin). In contrast to Cu^I ($Cu^{II/I}$ potential, ∼50 mV),[4] the distal Co^{II} ($Co^{III/II}$ potential, ∼300 mV) may not be an efficient electron donor for weaker oxidants (BrO_3^-), accounting for the different reactivities of ImCoTACNM (M = Co, Cu) toward BrO_3^-. Finally, unusually rapid degradation of ImCoTACNCo in the presence of H_2O_2 seems to eliminate the catalytic activity of this complex toward H_2O_2.

In contrast to ClO_2^-, H_2O_2, and BrO_3^-, all redox-active metalloporphyrins catalyze facile ($k_{max} > 10^5$ $M^{-1}s^{-1}$) 2e reduction of

IO_4^- (to IO_3^-). The onset of the catalysis correlates with the $M^{III/II}$ potential, indicating rapid catalytic turnover, limited by the concentration of the catalytically active M^{II} form.

In summary Mn, Fe, and Co porphyrins were found to be active catalysts for $4e/4H^+$ reduction of ClO_2^-; this activity correlates well with that measured in reduction of H_2O_2. The reactivity-enhancing effect of imidazole ligation and the distal metal was observed in several cases. The metalloporphyrins studied were inert to ClO_x^- ($x = 3, 4$) and IO_3^- but catalyzed $2e/2H^+$ reduction of IO_4^-; $6e/6H^+$ reduction of BrO_3^- was observed for Fe and Mn porphyrins and a CoCu derivative.

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

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