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ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · MAY 2014

Impact Factor: 12.11 · DOI: 10.1021/ja5021684 · Source: PubMed

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Electrocatalytic O_2 Reduction by [Fe-Fe]-Hydrogenase Active Site Models

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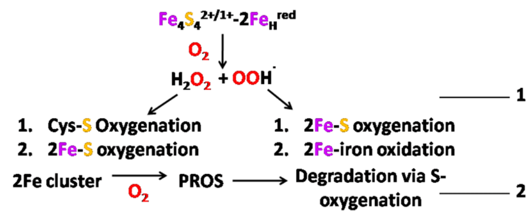
Supporting Information

ABSTRACT: The instability of [Fe-Fe]-hydrogenase and its synthetic models under aerobic conditions is an inherent challenge in their development as practical H_2 producing electrodes. The electrochemical oxygen reduction reaction of a series of synthetic model complexes of the [Fe-Fe] hydrogenase is investigated, and a dominant role of the bridgehead nitrogen in reducing the amount of partially reduced oxygen species (PROS), which is detrimental to the stability of these complexes, is discovered.

The natural [Fe-Fe]- and [Ni-Fe]-hydrogenases (H_2ases) as well as a hybrid construct composed of the apo-[Fe-Fe]-H_2ase outfitted with a synthetic 2Fe subsite can efficiently catalyze the conversion of H^+ to H_2 under optimal physiological conditions.[1−4] H_2ases are potential electrocatalysts for H_2/O_2 fuel cells due to their low overpotentials, high catalytic rates, and high turnover numbers.[5,6] However, their sensitivity to O_2 has limited practical applications as electrode materials for H_2/O_2 fuel cells, an area of great contemporary importance.[7−9] The low-valent reduced [Fe-Fe]-H_2ase active site reduces O_2 to produce partially reduced oxygen species (PROS) such as O_2^- and H_2O_2 which can rupture the nearby Fe-S clusters involved in delivering the electrons necessary to reduce H^+ to H_2 and/or stay bound to the cluster after electron transfer from the 2Fe2S cluster.[10] Computational investigations have suggested that the thermodynamics of O_2 binding to the cluster is indeed favorable, and there are gas channels available for O_2 to access the active site.[11,12] Investigations of intermediates formed during reaction of O_2 with the active site suggest formation of O_2 bound intermediates at the 2Fe subsite which lead to formation of PROS which degrades the Fe_4S_4 cluster.[12] The reduction of O_2 to O_2^- as well as H_2O_2 at the 2Fe site has been computationally predicted.[11] Scheme 1 displays these hypothesis that have driven the design of biomimetic research, oriented toward understanding the potential for oxygen damage of the 2Fe subsite of the H-cluster, i.e., the [Fe-Fe]-H_2ase active site. Direct electrochemical reduction of O_2 in an aqueous medium by synthetic analogues of H_2ases has, to our knowledge, not yet been investigated.

Over the last two decades numerous synthetic analogues of 2Fe subsite of the [Fe-Fe]-H_2ase active site have been reported.[13] Recently, some of these have been proven to be efficient catalysts for proton reduction under acidic aqueous conditions.[14−17] The catalytic abilities of these models, in both aqueous and organic mediums, are limited to strictly anoxic conditions as the low-valent iron as well as the bridging thiolate ligands, for an alkane dithiolato ligand, were found to be prone to oxygenation.[18] We posit that investigation of the ORR activity of a synthetic analogue of the [Fe-Fe]-H_2ase active site, that is a proven efficient hydrogen evolution reaction (HER) catalyst in aqueous medium, may provide valuable insight aiding design of better oxygen-tolerant H_2 evolving catalysts. Here, we describe the O_2 reduction reaction catalyzed by three [Fe-Fe]-H_2ase active site models with different bridgehead substituents in the S to S linker (Figure 1). The first two models (**1** and **2**) bear dimethyl-azadithiolate (ADT), and the model **3** contains the propane-dithiolate (PDT) bridging ligand. The results demonstrate a major role played by the bridgehead nitrogen in lowering the amount of H_2O_2 produced during O_2 reduction, offering longer HER catalyst lifetime under ambient aerobic conditions.

Scheme 1. PROS Generation by [Fe-Fe]H_2ases and Its Possible Reactivities



Complex **1** has been recently demonstrated to effect facile H_2 production under anoxic acidic aqueous solutions with a turnover frequency as high as 6000 s^{-1}, turnover numbers as high as 10^8, and faradaic efficiencies >95%.[15] Under aerobic conditions the same catalyst shows significantly lower electrolytic current (Figure S1, green) and a faradaic efficiency of only 65%. The decay of electrocatalytic current indicates decay of the catalyst under oxic conditions, and the lower faradaic yield suggests the presence of competitive electrocatalytic O_2 reduction. Under anoxic conditions the cyclic voltammogram (CV) of **1** physisorbed on a pyrolytic edge-plane graphite electrode (EPG) shows two consecutive quasi-reversible redox couples ($E_{1/2}$) at −0.24 and −0.37 V vs NHE at pH 7 that correspond to the $[\mathbf{1}]^-$ and $[\mathbf{1}]^{2-}$ states, respectively.[15] Under oxic environments a clear mass transport-limited current response to the added O_2 occurs at −0.26 V, indicating that **1**

Received: March 6, 2014
Published: May 20, 2014

dx.doi.org/10.1021/ja5021684 | J. Am. Chem. Soc. 2014, 136, 8847−8850

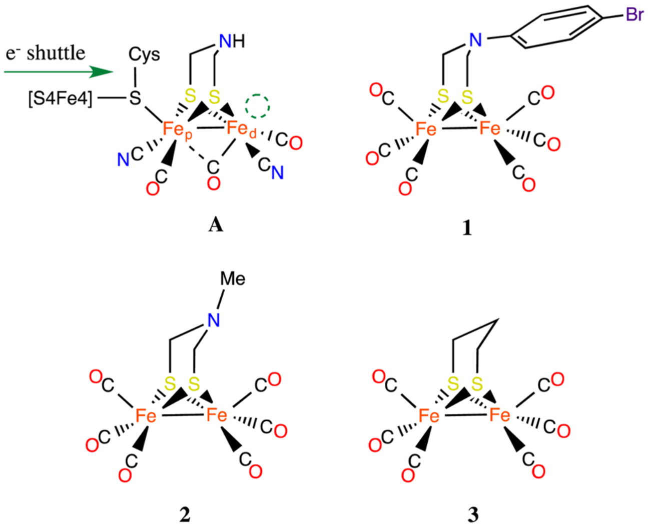


Figure 1. Active site structure of the [Fe-Fe]-H_2ase enzyme (A). Dinuclear iron models with $Fe_2S_2(CO)_6$ core bearing ADT (**1** and **2**), when an aromatic group is attached to the N in **1** and an alkyl group in **2**. Complex **3** contains PDT bridging moiety.

in the Fe^I–Fe^0 state can catalyze oxygen reduction reaction (ORR) (Figure 2A). The catalytic current increases linearly with O_2 concentration indicating a pseudo-first-order kinetics of ORR (Figure S2).

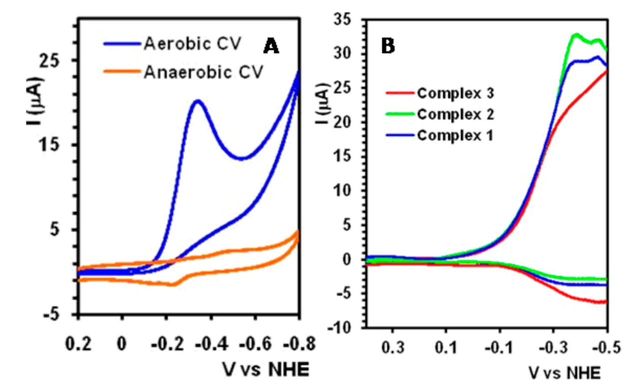


Figure 2. (A) CV of **1** under anaerobic (100 mV/s) and aerobic (50 mV/s) environment at pH 7. (B) RRDE of complexes **1**–**3** in 0.5 M H_2SO_4 (50 mV/s).

Rotating ring disk electrochemistry (RRDE) is an analytical technique that is used to quantitatively estimate H_2O_2 produced during ORR.[19,20] In a RRDE set up a Pt ring electrode encircles the working EPG electrode where any H_2O_2 formed, due to the incomplete reduction of O_2 by **1**, and is reoxidized to O_2 generating an oxidation current (Figure 2B, red). For model complexes **1**–**3**, the Pt ring shows an oxidation current which profiles similarly to the ORR current with the applied potential (Figure 2B). The amount of H_2O_2 produced during O_2 reduction by **1** is determined to be 57%. Similarly the amount of the PROS is estimated to be 62% for **3** and 49% for **2** at pH 7. Release of reactive H_2O_2 in significant quantities can degrade the catalyst and account for the decrease of HER activity with time during bulk electrolysis experiments, performed in aerobic solution. FTIR data on the electrode before and after ORR clearly show decrease in the carbonyl peak intensities (Figure S3A) and increase in peak intensities at 800 and 1020 cm^{-1} (S-O stretches of RSO_2^- and RSO_3^- groups, Figure S3B)[18] suggesting degradation of the catalyst via thiolate oxidation by the H_2O_2 produced during ORR. XPS data obtained after ORR show S $2p_{3/2}$ ionizations at 168–170 eV characteristic of RSO_2^- and RSO_3^- groups in addition to the thiolate peak at 162.5 eV (Figure S3C).[15,18e] In the presence of 25 μM catalase, a heme enzyme responsible for dismutating H_2O_2 to O_2 and H_2O at very high rates, the ORR current of **1** is sustained over a longer period (Figure S4) directly implicating the role of H_2O_2 produced in cluster degradation.

The linear sweep voltammetry data collected at various pH's show minimal variation in the onset potential for O_2 reduction (Figures S5–S7). The reduction of these complexes from their native Fe(I)Fe(I) redox level to the reactive Fe(I)Fe(0) step does not involve a proton and may be the pH-independent potential-determining step involved in ORR. Alternatively, the amount of PROS is lowered significantly as the pH of the solution is lowered and reaches a limiting value around pH 2–3 (Figure 3). The amount of H_2O_2 for **2** (the complex bearing an

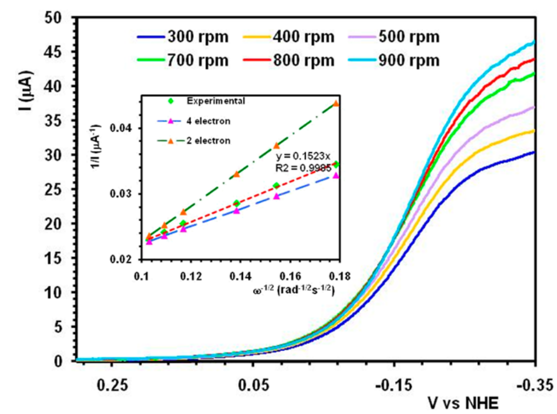


Figure 3. RDE for the complex **1** on EPG electrode in 0.5 M H_2SO_4 solution at a different rotation speed in aerobic environments. Inset: K-L plot ($1/I$ vs $\omega^{-1/2}$).

alkylamine bridge) is lowered to 21% in 0.5 M H_2SO_4 solution relative to 49% at pH 7. The amount of H_2O_2 produced by **1** is lowered to 29% from 57% as the pH is lowered from 7 to 0. Similarly for **3** the amount of H_2O_2 is lowered to 45% at pH = 0 relative to 62% at pH 7. Note that the decrease in H_2O_2 with pH 5 to pH 4 is observed for a carbon-bridged (**3**), an alkylamine-bridged (**2**), and an aromatic amine-bridged (**1**) complex. However, the magnitude of decrease is minimum for the carbon-bridged (**3**) and maximum for the alkylamine-bridged (**2**) complex. These data suggest that the decrease of PROS observed between pH 5.5–4.5 may not originate from the bridgehead atom; however, the gradual decrease below pH 4 arguably does.

Koutecky–Levich (K-L) analysis of the electrochemical reduction of O_2 by **1** in 0.5 M H_2SO_4 solution (Figure 4) indicates that the number of electrons transferred to the substrate O_2 is 3.5 ± 0.1.[19] The partial reduction of O_2 to H_2O_2 is responsible for lowering the number of electrons delivered to O_2 from its ideal value of 4. A value of 3.5 implies 75% $4e/4H^+$ reduction of O_2 to H_2O, i.e., 25% reduction to H_2O_2. This is in good agreement with the observation of 29% PROS observed for the same complex in the RRDE experiments at the same pH. Unfortunately, the number of electrons delivered to the substrate, O_2, could not be exactly determined using K-L analysis, because at higher pHs the H_2O_2 generated (~50%)

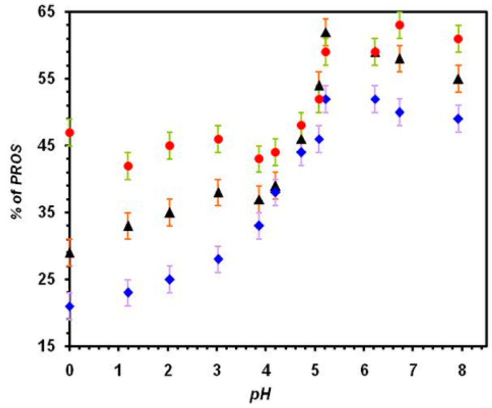


Figure 4. Amount of H_2O_2 produced at −0.4 V vs NHE at various pHs with 1 (black ▲), 2 (blue ◆) and 3 (red ●).

degrades these complexes before a K-L analysis can be performed. Nevertheless, the RRDE result suggests that under neutral conditions ∼50% of the O_2 is directly converted to water, a $4e^-$ reduction process ($O_2 + 4e^- + 4H^+ \rightarrow 2\ H_2O$), and the rest contributes to the PROS formation (∼50%). Note that while a $4e/4H^+$ reduction of O_2 to H_2O entails an inner-sphere mechanism, the reduction of O_2 to H_2O_2 does not. Unlike **3**, where the H_2O_2 produced sharply decreases from 60% in pH 5.1 to 43% at pH 4 and then stays constant at lower pHs, the H_2O_2 produced by **1** and **2** gradually reduces with lowering of the pH after the initial sharp decrease between pH 5 and 4. The H_2O_2 produced for **2**, with an alkylamine (higher pK_a) bridge, is lower relative to **1** which has an aromatic amine bridge (lower pK_a). These sets of data imply that the sharp drop in H_2O_2 between pH 5 and 4 is inherent to the 2Fe cluster, but the gradual drop from pH 4 to pH 0 is due the amine bridge. Note that release of less H_2O_2 (inner-/outer-sphere) implies a greater extent of $4e^-/4H^+$ reduction of O_2 to H_2O.

These experimental data can be rationalized by considering the terminal binding of O_2 to singly reduced diiron complex, as reported previously,[10] and formation of $Fe^I{-}O_2^-$ type adducts as intermediates (Figure 5) in the ORR. DFT calculations (BP86/

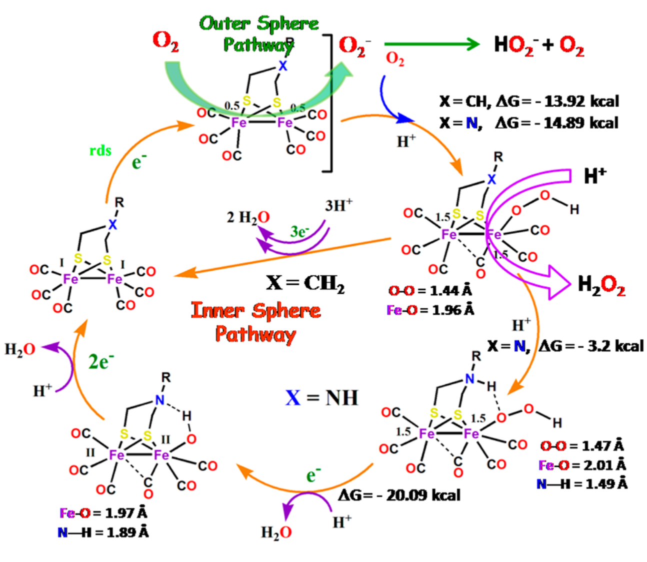


Figure 5. Proposed mechanistic scheme for O_2 reduction by ADT-bridged Fe-Fe hydrogenase mimics (e^- are obtained from the electrode and H^+ are obtained from solution).

6-311g* in Gaussian 03)[22−24] of the reduced Fe(1)-Fe(0) state indicate that it is best described as a Fe(0.5)Fe(0.5) system as the unpaired electron is added to an unoccupied Fe-Fe σ^* orbital of the resting Fe(1)-Fe(1) state. Thus, the spin density resulting from the reduction is evenly delocalized on both the Fe centers (Figure 6, left). This leads to decrease in bond order of the Fe-Fe

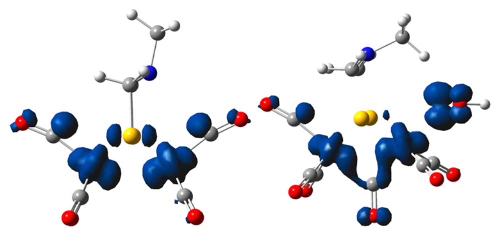


Figure 6. Spin density on the reduced Fe(0.5)Fe(0.5) cluster (left) and Fe(1.5)Fe(1.5)-OOH species (right).

bond from 1 in the Fe(1)Fe(1) state to 0.5 in the Fe(0.5)Fe(0.5) state.[24] The Fe-Fe distances increase from 2.55 Å in the Fe(1)Fe(1) state to 2.71 Å Fe(0.5)Fe(0.5) state consistent with the above proposal. These calculations indicate that O_2 binding is only possible if it is associated with a protonation (Figure 5). The energy for this proton-assisted O_2 binding varies little with the nature of the bridgehead atom (−13.92 kcal/mol for CH_2 and −14.89 kcal/mol for NMe, Figure 5). Judging by the O-O bond (1.44 Å, Table S1) and the lack of significant spin density on the O_2 unit (Figure 6, right), the resultant species is best described as a peroxide, i.e., O_2 is reduced by two electrons.[11] The calculated spin density (Figure 6, left) is delocalized uniformly on both the Fe centers such that it is best described as Fe(1.5)Fe(1.5)-OOH. The Fe-Fe bond length in the Fe(1.5)Fe(1.5) species is 2.71 Å, similar to that of the Fe(0.5)Fe(0.5). This is because as the Fe(0.5)Fe(0.5) state is oxidized by two electrons to a Fe(1.5)Fe(1.5) state by O_2; one electron is removed from the singly occupied Fe-Fe σ^* orbital and the other from the doubly occupied Fe-Fe σ orbital. The Fe-Fe bond order is thus 0.5 for both Fe(0.5)Fe(0.5) and Fe(1.5)Fe(1.5) states resulting in 0.2 Å longer Fe-Fe distances relative to the Fe(1)Fe(1) state.

The initial drop in H_2O_2 production between pH 5.5 and 4.5, independent of the bridgehead atom, likely represents the H^+-assisted oxidation of the Fe(0.5)Fe(0.5) state to form the Fe(1.5)Fe(1.5)-OOH species (Figure 5). The computations indicate that binding of O_2 shifts one of the terminal CO ligands to a bridging position in this intermediate (Figure 6, right). This is the first intermediate of the inner-sphere $4e/4H^+$ ORR mechanism which leads to lowering of H_2O_2 production. Hydrogen bonding between the -OOH and the bridgehead nitrogen may explain lower H_2O_2 production by **1** and **2** relative to **3** at pH 7. Further protonation of the NMe group is exothermic and activates the Fe-OOH unit for cleavage via hydrogen bonding as indicated by elongation of the O-O bond to 1.47 Å (Table S1). Interestingly this effect is analogous to a terminal hydride intermediates involved in proton reduction.[13c] Further reduction of these species to cleave the O-O bond, resulting in $4e/4H^+$ reduction of O_2, will require both electrons and protons. The fact that the PDT-bridged species does not show any decrease in H_2O_2 production below pH 4 (i.e., no increase in the extent of $4e/4H^+$ reduction of O_2) and that the ADT-bridged complexes do is consistent with the observed role of the hydrogen bonding from the protonated bridgehead nitrogen in aiding O-O bond cleavage. The weakening of the O-O bond will promote O-O bond cleavage favoring $4e/4H^+$

dx.doi.org/10.1021/ja5021684 | J. Am. Chem. Soc. 2014, 136, 8847−8850

reduction of O_2, thus producing less H_2O_2 as observed experimentally. This stabilization via H-bonding is not available for the PDT-bridged complex **3**. Hence, no further reduction of the amount of H_2O_2 is observed below pH 5. The stabilization of the terminal hydroperoxide (-OOH) species by H-bonding is further supported by the fact that the alkylamine-bridged **2**, with a greater availability of the nitrogen lone pair, exhibits greater 4*e*/4H$^+$ reduction of O_2 and less H_2O_2 than the aromatic amine-bridged complex **1**. An ~20% H_2O_2 production implies that the proton-assisted hydrolysis of the Fe(1.5)Fe(1.5)-OOH intermediate competes with O-O bond cleavage under acidic conditions. The H_2O_2 production step shows a solvent isotope effect of 2.08 ± 0.02 (Figure S8) consistent with the above proposal. The O-O bond cleavage requires two electrons, derived either from the cluster or from the electrode (Figure S9) and a proton. These calculations indicate that the most energetically favored path involves extraction of one electron from the cluster (resulting In a Fe(2)Fe(2) state and another from the electrode.

In summary, the electrocatalytic O_2 reduction by synthetic models of the [Fe-Fe]-H_2ase, one of these complexes, **1**, is known to produce H_2 under anoxic acidic conditions over 12 h without appreciable decay, are investigated. The results show that these complexes, irrespective of the nature of the bridge, reduce O_2 in their Fe(0.5)Fe(0.5) state producing >50% H_2O_2 above pH 5 leading to catalyst decay during HER under aerobic conditions. Although these clusters do not react with H_2O_2 in their oxidized Fe(I)Fe(I) state (Figure S10), they degrade via Fe_2S_2 oxidation (Scheme 1) by H_2O_2 generation during the reaction of O_2 with the reduced cluster. The presence of an antioxidant, catalase, also increased the longevity of the catalyst in an oxic environment. The extent of H_2O_2 production is significantly lowered at acidic pH's and attenuated by the nature of the bridging ligand; vis-a-vis a *N*-alkyl ADT bridge produces the lowest amount of H_2O_2 under acidic conditions. The reduction in H_2O_2 production during O_2 reduction at low pHs, facilitated by the hydrogen bonding from the protonated bridgehead nitrogen atom, observed in these synthetic complexes demonstrates that the bridgehead nitrogen atom may protect the natural active site as well, i.e., a protonated ADT ligand may be an intrinsic mechanism for protection of the H-cluster from oxidative damage by H_2O_2 produced from competitive O_2 reduction.

■ ASSOCIATED CONTENT

Supporting Information

Detailed materials and methods and full ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is funded by Department of Atomic Energy, India, (2011/36/12-BRNS) (A.D.) and National Science Foundation CHE 1266097 and R. A. Welch FoundationA-0924 (M.Y.D.). S.D., B.M., and P.K.D. thank CSIR-SRF fellowship program.

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