

Electrocatalytic Multielectron Nitrite Reduction in Water by an Iron Complex

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 FeN_5H_2 catalyzes ammonium production by disproportionation of hydroxylamine with concomitant formation of nitrous oxide and dinitrogen. These results are a rare example of multielectron electrocatalytic nitrite reduction by an iron complex near neutral pH.

KEYWORDS: ammonia synthesis, electrocatalysis, hydroxylamine disproportionation, hydroxylamine synthesis, nitrite reductase

N itrite (NO_2^{-}) plays an important role in the global nitrogen cycle, where its transformation leads to a variety of products along different pathways. Human activity has greatly disrupted this bio-geochemical cycle, with widespread effects, including eutrophication and contamination of groundwater.^{1,2} Studying the reactivity of NO_2^{-} will improve our understanding of its interconversions relevant to the nitrogen cycle. Furthermore, the reduction of the oxyanions of nitrogen is a route to transforming groundwater contaminants into useful products such as hydroxylamine (NH₂OH) and ammonia (NH₃) or removal by forming dinitrogen (N₂).³⁻⁶

A biomimetic approach to studying the activation of NO_2^- has been taken through the investigation of Cu or Fe complexes that mimic the reactivity of nitrite reductases, which yield nitric oxide (NO) (Cu or Fe (heme) enzymes, eq 1) or ammonium (NH₄⁺) (heme or siroheme enzymes, eq 2).^{4,7} Copper complexes have been reported to catalyze the reduction of NO_2^- to NO, nitrous oxide (N₂O), NH₂OH, and/or NH₄^{+,8,9} Among iron-containing compounds that transform NO₂⁻ to reduced products, ^{10–13} iron porphyrins have been reported as electrocatalysts for the reduction of NO₂⁻to mixtures of N₂O, NH₂OH, and NH₄⁺, where product distribution depends on applied potential, reaction time, and pH.^{12,13}

$$NO_2^- + 2H^+ + 1e^- \to NO + H_2O$$
 (1)

$$NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O$$
 (2)

Although cobalt is not implicated in Nature's transformations of NO_2^- , a number of cobalt complexes featuring a CoN₄ center are particularly active and well-studied catalysts for NO₂⁻ reduction.^{9,14-21} Ligand scaffolds represented in this group include cyclams,²¹ the cyclam analog, 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene (DIM),^{14,15,19} phthalocyanines,⁹ diimine-dioximes,¹⁸ peptides¹⁶ and porphyrins.^{17,20} Some of these catalysts also facilitate the reduction of nitrate (NO₃⁻).^{9,14,19-21} Hydroxylamine and $NH_4^{+9,14-17,19-21}$ are common reduction products, although a cobalt diimine-dioxime complex produces N2O.18 Understanding the basis for product selectivity is an area of interest. Product distribution has been found to depend on catalyst structure,^{14,15} mechanism,¹⁸ applied potential,^{9,17,20} and pH.²⁰ In many of these systems, however, the effect of pH is difficult to assess due to the absence or interference of a buffer, leading to large pH changes during the reaction.^{14,15,20,21} This pH change impacts acidic disproportionation of NO2⁻ to NO and $NO_3^{-,11,12,17,22-24}$ the differing reactivity of NH_2OH and its protonated form, NH_3OH^+ ,^{12,20} and catalyst stability.^{11,17}

Herein, we report catalytic reduction of NO_2^- to NH_2OH and NH_4^+ by an iron complex near neutral pH in the presence of 3-(*N*-morpholino)propanesulfonate (MOPS) buffer. This complex (FeN₅H₂) consists of an iron center coordinated by a

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macrocyclic ligand, 2,13-dimethyl-3,6,9,12,18pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (Figure 1)²⁵⁻²⁸ and was previously reported to catalyze the reduction of carbon dioxide to formic acid with 75–80% faradaic efficiency (FE) in DMF at -1.25 V vs SCE.²⁹



Figure 1. Structure of FeN_5H_2 as synthesized. Outer-sphere perchlorate anion is not shown.

The reactivity of FeN_5H_2 toward NO_2^- was initially investigated by cyclic voltammetry (CV) in the presence of MOPS buffer at pH 7.2. The CV of FeN_5H_2 (Figure 2)



Figure 2. Cyclic voltammograms (100 mV/s) of 50 mM MOPS in water (pH 7.2) with KCl or NaNO₂ and FeN₅H₂ added as indicated in the legend. The third scan is shown for each experiment.

features a single reversible redox event with a midpoint potential $(E_{1/2})$ of -0.10 V vs Ag/AgCl (1 M KCl)³⁰ attributed to the chemically and electrochemically reversible $Fe^{III/II}N_5H_2$ couple (Figure 2).³¹ When NO₂⁻ is present, this reversible feature persists, but an additional irreversible feature is seen at half-wave potential $E_{p/2}$ = -0.98 V when 50 mM MOPS, 100 mM NaNO₂, and 500 μ M FeN₅H₂ are present. The peak current for the irreversible feature has a linear dependence on [FeN₅H₂], [NO₂⁻], and [MOPS] before eventually leveling off at higher concentrations of each (Supporting Information Figures S1-S3). Solution pH also impacts peak current, with lower pH translating to a higher current response (pH 6.0–8.6; Figure S4). The $E_{p/2}$ value also depends on [FeN₅H₂], [NO₂⁻], and [MOPS] (Figures S1-S3). The scan-rate dependence of the reversible and irreversible features was also investigated (Figure S5); the plots of peak current vs the square root of the scan rate for both the reversible and irreversible features demonstrate a

linear relationship, consistent with these processes being homogeneous. $^{\rm 32}$

Controlled potential electrolysis (CPE) was carried out to determine whether the irreversible feature observed in CV corresponds to catalytic NO₂⁻ reduction and to identify the resulting product(s). CPE was performed at the half-wave potential of -0.98 V in the presence and absence of 500 μ M FeN₅H₂ in a solution containing 1.0 M NaNO₂ and 1.0 M MOPS at pH 7.2 over 1 h (Figures 3 and S6). With all



Figure 3. Controlled potential electrolysis at -0.98 V vs Ag/AgCl (1 M KCl) over 1 h of an aqueous solution containing 1.0 M NaNO₂ and 1.0 M MOPS at pH 7.2 with FeN₅H₂ as indicated in the legend.

components present, 70 C of charge was generated in 1 h.³³ Additionally, the solution pH increased from 7.2 to 7.5, despite the high buffer concentration, indicating significant proton consumption during the CPE experiment. In the absence of FeN_5H_2 , only a minimal charge (2.0 C) was passed and no measurable change in pH was observed (Table S1).

Following CPE, product identification was conducted. The presence of the six-electron-reduced product NH_4^+ was evaluated by the indophenol blue test³⁴ (Figure S7). Ammonium was formed with 8.1% FE. After confirming the presence of NH_4^+ , but accounting for only some of the charge passed, NH_2OH was assayed by redox titration with K_3 [Fe-(CN)₆].³⁵ Hydroxylamine is another multielectron reduction product, which is also a proposed intermediate for NH_4^+ formation from NO_2^- by nitrite reductase enzymes (Scheme 1).³⁶ Formation of NH_2OH was indeed found to occur with a FE of 91% in 1 h (TON = 65). In the absence of FeN₅H₂, no NH_4^+ or NH_2OH was detected.

The dependence of the product distribution between NH₄⁺ and NH₂OH on CPE applied potential was evaluated to compare to results reported for other catalysts^{9,12,13,17,20} (see Figure S8 for results of CPE at a range of potentials). One-hour CPE (500 μ M FeN₅H₂, 1.0 M MOPS, 1.0 M NaNO₂, pH 7.2) at -1.1 V passed 112 C with an FE of 6.8% for NH₄⁺ and 93% for NH₂OH, and at -1.3 V passed 188 C to yield an FE of 6.7% for NH₄⁺ and 89% for NH₂OH (Table S1 and Figure S9). While more charge was passed at lower potentials, product distribution was not significantly affected by applied potential. This observation contrasts with reports on electrocatalytic NO₂⁻ reduction to NH₂OH and NH₄⁺ by iron *meso*-tetrakis(4-sulfonatophenyl)porphyrin (Fe(TPPS))¹² and iron *meso*-tetrakis(N-methyl-4-pyridy1)porphyrin (Fe(TMPYP)).¹³

Scheme 1. Proposed Reaction Scheme for NO_2^- Reduction to NH_4^+ by Nitrite Reductases³⁶



The dependence of product distribution on potential seen for Fe(TPPS) was found to result from stepwise reduction of NO_2^- , where reduction of NH_2OH occurs at a low potential relative to its formation (Scheme 1).¹²

The effect of CPE time on product distribution also was evaluated. CPE of FeN₅H₂ (500 μ M FeN₅H₂, 1.0 M MOPS, 1.0 M NaNO₂, pH 7.2 at -0.98 V) was performed for 5 h, and [NH₂OH] and [NH₄⁺] were assayed (Figure S10). A total of 128 C was passed, NH₂OH was formed with 64% FE, and NH₄ was formed with 18% FE (Table S1). A dependence of product distribution on time has been reported previously.^{12,20} For example, in the case of the Fe(TPPS) electrocatalyst, longer CPE times increasingly favor NH₄⁺ formation at the expense of NH₂OH.¹² The basis for this finding is that conversion of NO₂⁻ to NH₂OH is fast relative to reduction of NH₂OH to NH₄⁺.

The observation of increased FE for NH_4^+ and decreased FE for NH_2OH with time for Fe porphyrin catalysts is accounted for by relatively slow conversion of NH_2OH to NH_4^+ . To determine if a similar slow step is active here, a constant potential of -0.98 V was applied to 1.0 M NH_2OH and 1.0 M MOPS (pH 7.2) in the presence and absence of FeN_5H_2 for 5 h. In the absence of the iron catalyst, consumption of NH_2OH was observed, resulting in formation of NH_4^+ (75% FE; Figures S11 and S12).³⁷ Notably, addition of FeN_5H_2 did not enhance the amount of passed charge, indicating that FeN_5H_2 is not active toward *electrocatalytic* reduction of NH_2OH (Figures S12 and S13). However, this result suggests that the mercury electrode is active in this reaction.

Disproportionation of NH₂OH is another possible route to formation of $NH_4^{\, +}$ along with N_2 and/or ${\bar N}_2O.^{38-41}$ While uncatalyzed disproportionation of NH₂OH is minimized at the near-neutral pH used in our experiments,^{38,39} there are several examples of iron complexes that catalyze this reaction.^{12,39,40} It is worth noting that N2 and N2O would have eluded the detection methods utilized thus far. Adding 500 μ M FeN₅H₂ to a sealed reaction vessel containing 1.0 M NH₂OH in 1.0 M MOPS, pH 7.2 led to consumption of 1.5 mmol of NH₂OH over 5 h as determined by $K_3[Fe(CN)_6]$ titration.³⁵ NH₄⁺ was identified as a product by ¹⁴N NMR analysis (Figure S11).³⁷ A buildup of gaseous products was observed, and N₂O and N₂ were detected in the headspace by gas chromatography (GC) (Figure S14). The detection of N_2O was further confirmed by infrared spectroscopy (IR; Figure S15). (Note that NO is not detected as a product as shown in Supporting Information, Figure S16).³⁹⁻⁴¹ In the absence of FeN₅H₂, a minimal amount of N₂O is formed, as evidenced by the small N₂O peak that is seen in GC (Figure S14). No NH_4^+ is detected from NH₂OH disproportionation in the absence of catalyst, but its

detection in this experiment relies on NMR, which has relatively low sensitivity (Figure S11). Thus, FeN_5H_2 -catalyzed disproportionation of NH_2OH is a route to form NH_4^+ . Scheme 2 summarizes the pathways observed in a model consistent with our observations.

Scheme 2. Pathways Active during NO_2^- Reduction by $FeN_sH_2^{a}$



^{*a*}FeN₅H₂ electrocatalytically reduces NO₂⁻ to NH₂OH, which undergoes direct reduction by the Hg electrode to form NH₄⁺. In addition, NH₂OH undergoes FeN₅H₂-catalyzed disproportionation to form NH₄⁺, N₂O, and N₂.

Comparison of the dependence of FeN₅H₂ catalytic activity toward NO₂⁻ reduction on conditions highlights a number of unusual properties of FeN5H2 compared to other nitritereducing catalysts. For FeN5H2, product distribution is not dependent on potential, contrary to what has been seen for other iron-^{12,13} and cobalt-containing^{17,20} catalysts as well as metallophthalocyanines,⁹ likely because the FeN₅H₂-catalyzed conversion of NH2OH to NH4+, N2O, and N2 occurs via disproportionation and thus does not require an applied potential. Similar to Fe(TPPS),¹² here the product distribution depends on CPE time. For Fe(TPPS), this time dependence of the product distribution results from the electrocatalytic conversion of NO2⁻ to NH2OH being faster than the subsequent electrocatalytic conversion of NH₂OH to NH₄⁺, while here it is is attributed to the relatively slow formation of NH_4^+ from NH_2OH via FeN_5H_2 -catalyzed disproportionation, as well as NH₂OH reduction at the electrode. Interestingly, FeN₅H₂ shares a similar reactivity toward NH₂OH disproportionation as Fe(TPPS),¹² but this reactivity is not reported in cobalt-containing complexes confirmed to produce NH₂OH as an intermediate or product of NO₂⁻ reduction.^{17,20,21}

In summary, we observe FeN₅H₂-catalyzed reduction of NO₂⁻ to NH₂OH at high faradaic yield; the NH₂OH then undergoes FeN_5H_2 -catalyzed disproportionation to form NH_4^+ , N_2O , and N_2 .³⁹⁻⁴¹ Similar metal complex-catalyzed disproportionation pathways of NH₂OH (NH₃OH⁺) may play a role in determining product distribution for other reported catalysts for NO2⁻ reduction. FeN5H2 stands out as a rare example of an iron complex that catalyzes multielectron NO₂⁻ reduction near neutral pH, where uncatalyzed disproportionation reactions of both $\mathrm{NO_2}^-$ and the $\mathrm{NH_2OH}$ product are slow. Notably, the reactivity of FeN₅H₂ is supported by buffer, allowing for controlled-pH studies, in contrast with reported systems that do not use,^{20,21} or are inhibited by, buffers.^{14,15} Furthermore, the *requirement* that buffer be present to observe catalysis indicates a role of buffer in the reaction, as has been observed for catalysts for hydrogen production in water.^{42,43} In future work, we plan to leverage this buffer requirement and

utilize modifications of the ligand scaffold to gain insight into the mechanism of the observed reactivity and to further optimize activity. Investigation of the reduction of other oxyanion species also is planned.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c03600.

Experimental procedures, details on data analysis, additional electrochemical data, absorption and IR spectra, and tables of results (PDF)

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Notes

The authors declare no competing financial interest.

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