Linking Thermodynamics to Pollutant Reduction Kinetics by Fe$^{2+}$ Bound to Iron Oxides

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ABSTRACT: Numerous studies have reported that pollutant reduction rates by ferrous iron (Fe$^{2+}$) are substantially enhanced in the presence of an iron (oxyhydr)oxide mineral. Developing a thermodynamic framework to explain this phenomenon has been historically difficult due to challenges in quantifying reduction potential ($E_{H}$) values for oxide-bound Fe$^{2+}$ species. Recently, our group demonstrated that $E_{H}$ values for hematite- and goethite-bound Fe$^{2+}$ can be accurately calculated using Gibbs free energy of formation values. Here, we tested if calculated $E_{H}$ values for oxide-bound Fe$^{3+}$ could be used to develop a free energy relationship capable of describing variations in reduction rate constants of substituted nitrobenzenes, a class of model pollutants that contain reducible aromatic nitro groups, using data collected here and compiled from the literature. All the data could be described by a single linear relationship between the logarithms of the surface-area-normalized rate constant ($k_{SA}$) values and $E_{H}$ and pH values [$\log(k_{SA}) = -E_{H}/0.059 V - pH + 3.42$]. This framework provides mechanistic insights into how the thermodynamic favorability of electron transfer from oxide-bound Fe$^{2+}$ relates to redox reaction kinetics.

INTRODUCTION

Ferrous iron (Fe$^{2+}$) bound to iron (oxyhydr)oxides reduces oxidized pollutants,1−13 molecular oxygen,15−18 and nitrate19 far more quickly than aqueous Fe$^{2+}$ alone. Early work studying this phenomenon proposed that Fe$^{2+}$ forms surface complexes on iron oxide surfaces that have higher electron densities than aqueous Fe$^{2+}$, due to surface hydroxyl ligands serving as electron donors.20,21 Consequently, oxide-bound Fe$^{2+}$ was thought to have a more negative reduction potential ($E_{H}$) value than aqueous Fe$^{2+}$ in the same solution.20,22−24 More recently, however, two lines of reasoning have questioned the validity of this explanation. First, spectroscopic and microscopic analyses demonstrated that an Fe$^{2+}$ atom rarely forms a stable adsorbed species on iron oxides, but rather it becomes oxidized to an Fe$^{3+}$ atom and donates an electron into the bulk semiconducting iron oxide lattice.24−31 Second, the explanation implicitly assumes that relevant solutions must be in a state of thermodynamic disequilibrium, as all redox couples in a system at equilibrium have the same $E_{H}$ value. Using electrochemical measurements, our group recently confirmed that suspensions containing aqueous Fe$^{2+}$ and goethite or hematite do reach thermodynamic equilibrium, indicating that oxide-bound Fe$^{2+}$ and aqueous Fe$^{2+}$ reach the same $E_{H}$ value. An alternative hypothesis to explain this phenomenon is that the presence of an iron oxide alters the Fe$^{2+}$ oxidation product that forms and therefore the Gibbs free energy of the reaction.32−35 When aqueous Fe$^{2+}$ oxidizes in the absence of an oxide, it produces an aqueous Fe$^{3+}$ complex or a metastable iron oxide (e.g., ferrihydrite).36 In contrast, when Fe$^{2+}$ oxidizes in the presence of a crystalline iron oxide surface, it commonly produces a thermodynamically stable iron oxide (e.g., goethite or hematite) via epitaxial growth.15,37,38 Thermodynamically stable iron oxides (e.g., goethite and hematite) have more negative Gibbs free energies of formation than metastable iron oxides (e.g., ferrihydrite), and therefore the iron oxide is thought to make Fe$^{2+}$ oxidation and concomitant epitaxial oxide growth more exergonic (i.e., thermodynamically favorable).

This hypothesis is consistent with characterizations of oxides made before and after pollutant reduction reactions, but it remains unclear if it can be invoked to quantitatively explain trends in pollutant reduction kinetics. In theory, $E_{H}$ values of oxide-bound Fe$^{3+}$ should relate to the observed reaction rate constants ($k_{obs}$) in a predictable manner if an electron transfer event occurs during or before the rate-limiting step of the reaction.39−42 The goal of this study was to test the validity of this argument for the reduction of a model oxidized pollutant by oxide-bound Fe$^{2+}$. We characterized the free energy relationship that exists between reaction rate constants for nitrobenzene reduction as a function of the $E_{H}$ values of oxide-bound Fe$^{2+}$ and pH. We subsequently tested if the free energy
relationship could describe data compiled from the literature collected with other iron oxides and substituted nitrobenzenes. We focused on nitrobenzene and its substituted analogs for three reasons. First, there are many studies in which substituted nitrobenzenes have been reacted with oxide-bound Fe$^{2+}$, which provided us with relevant data to reinterpret. Second, the elementary steps in the reduction reaction substituted nitrobenzenes to the corresponding anilines have been extensively characterized, which allowed us to interpret $k_{obs}$ values in the context of elementary reaction steps. Third, nitrobenzene does not appreciably adsorb to iron oxides, which means that the disappearance rate of nitrobenzene can be assumed to be equal to the transformation rate.

MATERIALS AND METHODS

All experiments were conducted under anaerobic conditions in a glovebox (MBraun Unilab Workstation, 100% N$_2$, O$_2$ < 0.1 ppm). All lab supplies that came in contact with Fe$^{2+}$ were left under vacuum for at least 12 h in the exchange chamber and allowed to equilibrate with the N$_2$ atmosphere before use. Deionized water (Millipore Milli-Q system, resistivity > 18 MΩ-cm) was used to make all aqueous solutions. All liquid solutions were purged with N$_2$ (99.99%) for at least 3 h before being cycled into the glovebox, except for nitrobenzene. Approximately 2 mL of reagent grade nitrobenzene (Sigma-Aldrich) was cycled through the vacuum chamber in a small sealed container with little headspace and was used to make 5 mM and 25 mM stock solutions in deoxygenated methanol. Ferrous chloride (FeCl$_2$, Acros, anhydrous, 99%) from a sealed ampule was used to make Fe$^{2+}$ stock solutions that were kept not diluted. The electrode was cleaned periodically with 0.1 M HCl. All measurements of aqueous Fe$^{2+}$ were done using the 1,10-phenanthroline method.

All experiments were done in aqueous solutions containing 25 mM KCl (EM Science) and 25 mM pH buffer. The pH buffer used at pH values 6.0 and 6.5 was MES (2-N-morpholinoethanesulfonic acid acid monohydrate, pKa 6.1, Aresco, ≥99%), and the pH buffer used at pH 7.0 was MOPS (3-N-morpholinosopropanesulfonic acid, pKa 7.2, EMD Chemicals Inc., 100%). Note that past works have argued that the buffers used here may affect iron oxide–aqueous Fe$^{2+}$ interactions. This possibility was unfortunately unavoidable, as we needed to maintain a constant pH in the experiments. While carbonate has been recommended as an alternative buffer, our interpretation of published data (below) suggests that carbonate dramatically inhibits nitrobenzene reduction rates by oxide-bound Fe$^{2+}$.

Goethite Synthesis and Characterization. An established protocol was used to synthesize two batches of micrometer-scale goethite. We synthesized two batches of goethite because the first batch was exhausted prior to completing all experiments. After synthesis, the goethite was freeze-dried (Labconco benchtop freeze-drier), ground with a mortar and pestle, and sifted through a 200 mesh sieve (Humboldt). The purities of the goethite batches were confirmed using cryogenic $^{57}$Fe Mössbauer spectroscopy. The BET surface area of the first goethite batch was 30.9 ± 0.3 m$^2$/g (ASAP 2020 Automated Surface Area and Porosimetry System). The BET surface area of the second batch was assumed to be equal to that of the first based on previous experience with this synthesis procedure. Unfortunately, we exhausted the second batch of goethite before the BET surface area was measured. On the basis of our experience, this synthesis method reliably produces goethite with a specific surface area of ≈30 m$^2$/g.

Reduction Potential Measurements. We used mediated potentiometry to determine standard reduction potential ($E^\circ$) values for each batch of goethite using a previously published protocol. We prepared triplicate reactors with varied initial Fe$^{2+}$ concentrations (100, 200, 400, 800, 1000, 1500, or 3000 μM) and pH (6.0 or 7.0) values. After the addition of aqueous Fe$^{2+}$, the pH was readjusted to the initial value using 1 N KOH and/or HCl stock solutions because the slight changes on the order of approximately 0.1 pH units significantly affected measured and calculated $E^\circ$ values. After measuring the initial Fe$^{2+}$ concentration, we added goethite to the solutions to achieve a mass loading of 1 or 2 g/L. Reactors were covered with aluminum foil to avoid inadvertent photochemical reactions and mixed on a magnetic stir plate. After 1 h of mixing, a mediator compound (cyanomethyl viologen, $E^\circ_{\text{H}}$ = −0.14 V) was added from a 10 mM stock solution to reach a final concentration between 10 and 20 μM. The reactors were mixed for 24 h, then a final aqueous Fe$^{2+}$ measurement was made by filtering the solution through a 0.45 μm nylon syringe filter. We then performed a potentiometric measurement of the solution at two second intervals for 1 h with a Pt ring combined redox electrode (Metrohm) inside the glovebox. The $E^\circ$ value reported is the lowest value recorded during the 1 h measurement. Between measurements, the electrode was stored in 3 M KCl for ≥3 h to ensure the internal KCl solution was not diluted. The electrode was cleaned periodically with 0.1 M HCl, and calibrated approximately monthly using quinhydrone buffers prepared at pH 4.0 and 7.0 (Tokyo Chemical Industry Co., LTD). All measurements were made in reference to Ag/AgCl, and were subsequently converted to values in reference to the standard hydrogen electrode (SHE) based on the calibrations. To convert from concentrations to activities, activity coefficients for Fe$^{2+}$ were calculated according to reactor conditions using Visual MINTEQ, and values ranged from 0.48 to 0.52.

Nitrobenzene Reduction Experiments. We set up reactors containing aqueous Fe$^{2+}$ and goethite using the same approach as described for the reduction potential measurements, except that no mediator was added. In the reactors, we varied the total initial Fe$^{2+}$ concentration, goethite loading, and pH value. After an equilibration period of 24 h in which the goethite and Fe$^{2+}$ reacted, a sample was taken to measure the final aqueous Fe$^{2+}$ concentration. Next, the reaction was started by adding an aliquot of nitrobenzene stock solution to the reactor using a glass syringe to reach an initial concentration of approximately 10 μM. The reactor was sealed with a Teflon-lined septa and aluminum crimp cap. Samples were taken at predetermined time points using a needle and syringe and filtered through a 0.2 μm PTFE syringe filter into amber sample vials with PTFE-lined screw caps. Nitrobenzene and aniline were measured using high-pressure liquid chromatography (HPLC) with a Supelcosil LC-18 column using established methods.

Derivation of Free Energy Relationship. We derived a rate expression to relate the disappearance of nitrobenzene to changes of reduction potential and pH using a quasi-equilibrium assumption, which assumes that the reaction steps preceding the rate-limiting step reach equilibrium.

The reduction pathway of nitrobenzene is shown in Scheme 1, with the relevant iron oxidation reactions shown in Figure S1. The overall rate of nitrobenzene (compound 1 in Scheme 1)
disappearance during a surface-catalyzed pseudo-first-order reduction reaction can be described by
\[
\frac{d[1]}{dt} = -k_{\text{obs}}[1] = -k_{SA}[1]
\]  
(1)

where \( k_{\text{obs}} \) is the observed pseudo-first-order reduction rate constant (1/h); \( A \) is the reactive surface area of an iron oxide (m\(^2\)/L), which is calculated from the measured BET specific surface area; and \( k_{SA} \) is the surface-area-normalized reaction rate constant [L/(m\(^2\)h)].

Studies on the \(^{15}\text{N} \) kinetic isotope effects\(^{45-47} \) have indicated that the rate-limiting elementary step of the reduction of nitrobenzene (or substituted nitrobenzene) is the hydrolysis of \( \text{N,N-di-hydroxyaniline} \) \( 5 \) to nitrosobenzene \( 6 \) when the reductant is present in excess. If this is the case, the overall rate of nitrobenzene \( 1 \) disappearance would depend on the rate constant for reaction \( 5 \rightarrow 6, k_{5\rightarrow6} \) and the concentration of \( \text{N,N-di-hydroxyaniline} \) \( 5 \):
\[
\frac{d[1]}{dt} = -k_{5\rightarrow6}[5]
\]  
(2)

Setting eqs 1 and 2 equal to each other relates \( k_{SA} \) to \( k_{5\rightarrow6} \):
\[
k_{SA} = k_{5\rightarrow6} \frac{[5]}{[1]}
\]  
(3)

For this relationship to have practical utility, the concentration of \( 5 \) must be expressed as a function of the concentration of \( 1 \). Using the quasi-equilibrium method, the concentration of \( 5 \) could be mathematically derived based on the concentrations of species \( 1 \) to \( 4 \) using equilibrium expressions for reaction sequence \( 1 \Rightarrow 2 \Rightarrow 3 \Rightarrow 4 \Rightarrow 5 \) in Scheme 1 and the oxidation of \( \text{Fe}^{2+} \) to goethite (\( K_{\text{Fe}^{2+}=a\text{FeOOH}} \) in eq 4e derived from the half reaction shown in eq 12 below):

\[
K_{\text{Fe}^{2+}=a\text{FeOOH}} = \frac{[\text{H}^+]^3}{[\text{Fe}^{2+}]} \]  
(4e)

Through a sequence of substitutions for transient species \( 1 \) to \( 4 \) for \( 5 \) and the assumption that electrons come from the oxidation of \( \text{Fe}^{2+} \) to \( \alpha\text{-FeOOH} \), eq 3 can be transformed to an interpretable relationship:

\[
k_{SA}[1] = k_{5\rightarrow6}[5]
\]  
(5a)
\[
=k_{5\rightarrow6} K_{4\rightarrow5} [4] [\text{H}^+]
\]  
(5b)
\[
=k_{5\rightarrow6} K_{4\rightarrow5} K_{3\rightarrow4} K_{\text{Fe}^{2+}=a\text{FeOOH}} [3] \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}
\]  
(5c)
\[
=k_{5\rightarrow6} K_{4\rightarrow5} K_{3\rightarrow4} K_{\text{Fe}^{2+}=a\text{FeOOH}} K_{2\rightarrow3} K_{1\rightarrow2} \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^3}
\]  
(5d)
\[
k_{SA} = k_{5\rightarrow6} K_{4\rightarrow5} K_{3\rightarrow4} (K_{\text{Fe}^{2+}=a\text{FeOOH}})^2 K_{2\rightarrow3} K_{1\rightarrow2} \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^3}
\]  
(5e)

The observable reaction rate constant for nitrobenzene reduction will therefore depend on the pH and \( \text{Fe}^{2+} \) concentration as well as the equilibrium constants for reactions \( 1 \Rightarrow 2, 2 \Rightarrow 3, 3 \Rightarrow 4, \) and \( 4 \Rightarrow 5 \).

While the electron transfer reactions involving the oxidation of \( \text{Fe}^{2+} \) to an oxide (in this case, goethite, \( \alpha\text{-FeOOH} \)) can be expressed in terms of an equilibrium constant (\( K_{\text{Fe}^{2+}=a\text{FeOOH}} \)), representing them in terms of \( E_H \) values is more familiar and practical in the context of redox reactions. The Nernst equation for the goethite-\( \text{Fe}^{2+} \) half reaction can be written in the following form (see eqs 12 and 13 below for more details):

\[
E_H = E_H^0 - \frac{RT}{F} \ln \left( \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^3} \right)
\]  
(6)

The Nernst equation can be re-expressed in terms of \( K_{\text{Fe}^{2+}=a\text{FeOOH}} \) which is inverted because the equilibrium constant is for the oxidation reaction:

\[
E_H^0 = \frac{RT}{F} \ln \left( \frac{1}{K_{\text{Fe}^{2+}=a\text{FeOOH}}} \right)
\]  
(7)
We initially considered the Nernst equation:

\[
E_H = \frac{RT}{F} \ln \left( \frac{1}{K_{Fe^{3+}_{aq} \rightleftharpoons FeOOH_{s}}} \right) - \frac{RT}{F} \ln \left( \frac{[Fe^{2+}_{aq}]}{[H^+]^{2}} \right) \tag{8}
\]

Solving for \( K_{Fe^{3+}_{aq} \rightleftharpoons FeOOH_{s}} \) yields

\[
K_{Fe^{3+}_{aq} \rightleftharpoons FeOOH_{s}} = \exp \left( -\frac{F}{RT} E_H \right) \left[ \frac{[H^+]^{2}}{[Fe^{2+}_{aq}]} \right] \tag{9}
\]

Substituting eq 9 into eq 5f yields a relationship in which \( k_{SA} \) can be related to \( E_H \):

\[
k_{SA} = k_{5a} K_{4a=5} K_{3a=4} K_{2a=3} K_{1a=2} \left[ \frac{[H^+]^{2}}{[Fe^{2+}_{aq}]} \exp \left( -\frac{F}{RT} E_H \right) \right]^{2} \tag{10a}
\]

\[
k_{SA} = k_{5a} K_{4a=5} K_{3a=4} K_{2a=3} K_{1a=2} \exp \left( \frac{2F}{2.303RT} E_H \right) \left[ [H^+]^{2} \right] \tag{10b}
\]

Taking the log of both sides of the equation yields

\[
\log(k_{SA}) = \log(k_{5a} K_{4a=5} K_{3a=4} K_{2a=3} K_{1a=2}) \left( d - \frac{2F}{2.303RT} E_H - 2 \cdot pH \right) \tag{10c}
\]

which at room temperature (25 °C) simplifies to

\[
\log(k_{SA}) = -2 \cdot \frac{E_H}{0.059 V} - 2 \cdot pH + d \tag{11}
\]

Note that this derivation can also be done in terms of the aqueous Fe\(^{3+}\) activity based on the solubility of the iron oxide present.\(^{32}\)

### RESULTS AND DISCUSSION

**Quantification of Goethite–Aqueous Fe\(^{2+}\) Values.** We initially confirmed that \( E_H \) values of suspensions containing goethite (\( \alpha-FeOOH_{s} \)) and aqueous Fe\(^{3+}\) (\( Fe^{3+}_{aq} \)) were consistent with the following half-reaction and corresponding Nernst equation:

\[
\alpha - FeOOH_{(s)} + e^{-} + 3H^{+} = Fe^{2+}_{(aq)} + 2H_{2}O \tag{12}
\]

\[
E_H = E_{H}^{0} - \frac{RT}{F} \ln[Fe^{3+}_{aq}] + \frac{3RT}{F} \ln[H^{+}] \tag{13}
\]

where brackets denote activities. At 25 °C, eq 13 simplifies to

\[
E_H = E_{H}^{0} - 0.059 V \cdot \log[Fe^{3+}_{aq}] - 0.177 V \cdot pH \tag{14}
\]

We measured \( E_{H}^{0} \) values of goethite suspensions over a range of total Fe\(^{3+}\) concentrations (100 to 3000 \( \mu M \)) at two pH values (6.0 and 7.0) using mediated potentiometry, a technique in which a soluble redox mediator is used to facilitate redox equilibration between a solution and a redox electrode performing a potentiometric measurement (Figure 1). Data for goethite from our previous work using the same method is shown for reference.\(^{32}\) We characterized two goethite batches made using identical synthesis routes because the first goethite batch was exhausted before all nitrobenzene experiments were completed. We fit the data for each goethite batch according to eq 14 by floating the \( E_{H}^{0} \) value and slope terms for \( Fe^{3+}_{aq} \) activity and pH using a least-squares multiple linear regression (Igor Pro software v7\(^{7} \), WaveMetrics). The activity coefficient for \( Fe^{3+}_{aq} \) was calculated according to reactor conditions. There was good agreement between the theoretical slope terms in eq 14 and those from the fitted regression (\( Fe^{3+}_{aq} \) term: theoretical, 0.059 V; batch 1, 0.071 \( \pm \) 0.008 (\( \pm \sigma \)) V; batch 2, 0.065 \( \pm \) 0.005 V; 0.177 V; batch 1, 0.177 \( \pm \) 0.008 V; batch 2, 0.165 \( \pm \) 0.005 V), confirming that the half-reaction in eq 12 accurately described the \( E_{H}^{0} \) values of the suspensions.

These data were fit to calculate \( E_{H}^{0} \) values for each batch of goethite. Since the deviations between the theoretical and measured slope terms were most likely due to experimental error, we used the theoretical slope values in eq 14 to fit the data using a linear regression. The fits, shown as dashed lines in Figure 1, yielded \( E_{H}^{0} \) values of 0.801 \( \pm \) 0.004 (\( \pm \sigma \)) V (\( r^2 = 0.98 \)) for batch 1 and 0.800 \( \pm \) 0.003 V (\( r^2 = 0.99 \)) for batch 2, which were within the range of previously reported values (0.72 to 0.84 V).\(^{56,57}\) The \( E_{H}^{0} \) values were both approximately 0.03 V higher than the values measured in our previous work using the same technique (0.768 \( \pm \) 0.001 V),\(^{32}\) which was likely due to slight differences between the goethite batches used in this study and our previous work. Since the \( E_{H}^{0} \) values of the two goethite batches used here were identical within error to each another, we could directly compare data collected for each batch. For all subsequent nitrobenzene reduction experiments, we calculated \( E_{H}^{0} \) values of each suspension based on the pH, \( Fe^{3+}_{aq} \) activity, and measured \( E_{H}^{0} \) value (0.800 V) according to eq 14.

**Role of \( E_{H} \) on Nitrobenzene Reduction Kinetics at pH 6.0.** We initially performed nitrobenzene reduction experiments at a single pH value (6.0) to simplify interpretation by eliminating pH-dependent effects on goethite–Fe\(^{3+}_{aq} \) \( E_{H} \) values (eq 14) and nitrobenzene reduction kinetics. To determine the relationship between \( k_{obs} \) values and initial \( E_{H} \) values of the goethite–Fe\(^{3+}_{aq} \) redox couple, we measured nitrobenzene reduction rate constants as a function of goethite concentration (0.5 to 4.0 g/L) and total Fe\(^{3+}_{aq} \) concentration (100 to 5000 \( \mu M \)). All the nitrobenzene reduction experiments could initially be described using a pseudo-first-order kinetic model (eq 1),
confirming that the reaction was first-order with respect to nitrobenzene (example data shown in Figure S2). In experiments that had relatively low initial Fe(aq) concentrations, reaction kinetics eventually deviated from what could be fit with a pseudo-first-order kinetic model, and therefore reported \( k_{obs} \) values were fit using only the portion of the data that yielded a linear fit between \( \ln(k_{obs}) \) vs time. In the experiments that went to completion, the mass balance of nitrobenzene reduced to aniline produced ranged from 98 to 120% (average = 107 ± 5%), and the molar ratio of Fe(aq) lost from solution to nitrobenzene reduced was 6.2(±2.8):1 (data shown in Figure S3), consistent with the expected ratio of 6:1 from the electron balance of the overall reaction (i.e., six electrons are needed to reduce one aromatic NO2 group to an NH2 group). The \( k_{obs} \) values among experiments were surface-area-normalized to account for differences in goethite loadings among experiments according to eq 1, as previously described in the literature.\(^5,6\)

We plotted a free energy relationship in which \( \log(k_{SA}) \) was related to the reaction’s thermodynamic driving force (i.e., the Gibbs free energy of the reaction, \( \Delta G_{\text{reaction}} \)). For redox reactions, \( \Delta G_{\text{reaction}} \) is typically expressed in terms of \( E_{\text{H}} \). Here, we used the \( E_{\text{H}} \) values of the goethite-Fe\(^{3+}\) redox couple divided by 0.059 V (i.e., by 2.303 \( RT/F \) when \( T = 25 \) °C). The data, shown in Figure 2 and tabulated in Table S1, exhibited a linear relationship (\( r^2 = 0.96 \)) with a slope of −0.99 ± 0.06. Note that \( E_{\text{H}}/0.059 \) V scales with \( \log(Fe^{2+}_{\text{aq}}) \) in a 1:1 ratio (eq 14), and therefore a slope of \( \approx −1 \) indicated that nitrobenzene reduction was first-order with respect to the Fe\(^{2+}\) activity:

\[
k_{SA} = k_{Fe^{2+}_{\text{aq}}}
\]

More generally, the fact that the slope was not zero was consistent with an electron transfer step being involved in the rate-limiting step and/or step(s) preceding the rate-limiting step of nitrobenzene reduction.\(^{40,42} \) The mechanistic implications of the slope value are discussed below. The practical significance of the slope is that the \( E_{\text{H}} \) values of the goethite-Fe\(^{3+}\) redox couple may be used as a parameter to predict trends in reduction rate constants of nitrobenzene, and likely other nitroaromatic compounds, for a single pH value. To understand if this relationship of \( k_{SA} \) with a reaction free energy trend was also valid at different pH values, we performed additional experiments.

**Effect of pH on Nitrobenzene Reduction Rates.** We measured nitrobenzene reduction kinetics at pH values of 6.5 and 7.0 for a subset of the reactor conditions tested at pH 6.0 (goethite concentrations of 1 and 2 g/L; total Fe\(^{3+}\) concentrations of 100 to 1000 \( \mu M \); data tabulated in Table S1). Since the pH value influences both the \( E_{\text{H}} \) value of the goethite-Fe\(^{3+}\) redox couple (eq 14) and the thermodynamic driving force dependence of nitrobenzene reduction rate constants, which involves proton transfer steps, we expected that \( \log(k_{SA}) \) values would vary as a function of both \( E_{\text{H}} \) and pH:

\[
\log(k_{SA}) = a \cdot \frac{E_{\text{H}}}{0.059 \text{ V}} + b \cdot \text{pH} + c
\]

where \( a, b, \) and \( c \) are constants. Since eq 16 contains two independent variables, its ability to describe the data cannot be easily visualized in a 2-dimensional plot. We fit the data using a multiple linear regression according to eq 16 while floating \( b \) and \( c \) and holding \( a \) equal to −1 (based on the results in Figure 2). The least-squares fit generated a pH slope term (\( b \)) of −1.06 ± 0.09 and an intercept term (\( c \)) of 3.6 ± 0.6 (\( \chi^2 = 0.67; n = 23 \)). The \( b \) value was \( \approx −1 \), which was the value that we used in subsequent analyses. To visually represent the quality of this fit, we plotted \( \log(k_{SA}) \) versus \( a \cdot E_{\text{H}}/0.059 \text{ V} + b \cdot \text{pH} \) with \( a = −1 \) and \( b = −1 \) (Figure 3, \( c = 3.12 ± 0.05, r^2 = 0.96 \)). The observation that the data was best described with a pH slope term that differed from 0 indicated that nitrobenzene reduction kinetics by goethite-bound Fe\(^{2+}\) were indeed pH-dependent, consistent with the reduction pathway of nitroaromatic compounds and the Fe\(^{2+}\) oxidation reaction.\(^{45,46} \)

Note that representing the data this way masks the actual pH-dependency of \( \log(k_{SA}) \), since \( E_{\text{H}} \) itself is a function of \( \text{pH} \) (eqs 13 and 14). When the \( E_{\text{H}} \) term is written out according to eq 14 and substituted into eq 16 with \( a \) and \( b \) equal to −1, it is clear that the reaction is second-order with respect to pH:

**Figure 2.** Log transformed surface-area-normalized reaction rate coefficient [\( \log(k_{SA}) \)] vs \( E_{\text{H}} \) values divided by 0.059 V of the goethite-Fe\(^{3+}\) redox couple at pH 6.0. The black line shows the linear fit with slope = −0.99 ± 0.06, intercept = −2.79 ± 0.06, \( r^2 = 0.96 \).

**Figure 3.** Relationship between \( \log(k_{SA}) \), pH, and \( E_{\text{H}} \) of the goethite-Fe\(^{3+}\) redox couple. The line shown is the fit with only the \( y \)-intercept term floated (\( c \) in eq 16 = 3.12 ± 0.05, \( r^2 = 0.96 \)).
log(k_{SA}) = \frac{E^{0}_{H}}{0.059 V} + \log([\text{Fe}^{2+}(aq)]) + 2 \cdot \text{pH} \tag{17}

The mechanistic significance that can be drawn from the pH-dependency is discussed below.

To test the robustness of this free energy relationship, we plotted previously reported log(k_{SA}) values for the reduction of nitrobenzene or substituted nitrobenzene compounds by Fe^{2+} bound to goethite (Figure 4).\textsuperscript{3,6,43} Since the rate of substituted nitrobenzene compounds depends on the substituent groups present, we normalized the data was: \textsuperscript{59} The method used to calculate \textit{E}_H values is provided in section S2. Reactor conditions varied between reported experiments: total Fe^{2+} ranged between 0.375 and 1.24 mM, goethite loading ranged between 0.025 and 1.54 g/L, BET specific surface areas of goethite ranged between 16.2 and 51 m\(^2\)/g, and pH values range between 6.1 and 7.97. The line shown is the fit from Figure 3.

Interestingly, the two outlier points in Figure 3 were collected using carbonate as a pH buffer,\textsuperscript{43} whereas all the other studies including ours used Good’s buffers. Note that we accounted for the fact that a portion (~7%) of the Fe^{2+} was complexed with carbonate (FeHCO\(_3\)) when calculating the activity of free Fe^{2+}(aq) from their data (Visual MINTEQ). Carbonate is known to decrease the amount of available reactive surface area on an iron oxide and decrease the extent of Fe^{2+} uptake.\textsuperscript{14} Since nitrobenzene reduction by Fe^{2+} is a surface-catalyzed reaction, the presence of carbonate explains the significantly lower log(k_{SA}) values observed in this study.

Free Energy Relationship for Nitrobenzene Reduction by Fe^{2+} and Different Iron Oxides. The consistent trend between log(k_{obs}) values and pH and \textit{E}_H values for goethite compelled us to explore the extent to which this relationship could be applied to reported data collected for other iron oxides, including hematite,\textsuperscript{3,6,60} lepidocrocite,\textsuperscript{3,8,60} ferrihydrite,\textsuperscript{3,8} and magnetite.\textsuperscript{9} Note that since the Gibbs free energy of formation of each oxide differs, the \textit{E}_H values for each oxide-Fe^{2+} redox couple also differ. We calculated \textit{E}_H of the oxide-Fe^{2+} redox couples according to the following half reactions and their corresponding Nernst equations:

Hematite:

\[ \frac{1}{2} \text{Fe}_2\text{O}_3(s) + 3\text{H}^+ + e^- \rightleftharpoons \text{Fe}^{2+}(aq) + \frac{3}{2}\text{H}_2\text{O} \tag{20a} \]

Lepidocrocite:

\[ \gamma \text{FeOOH}(s) + 3\text{H}^+ + e^- \rightleftharpoons \text{Fe}^{2+}(aq) + 2\text{H}_2\text{O} \tag{20b} \]

Ferrihydrite:

\[ \text{Fe(OH)}_3(s) + 3\text{H}^+ + e^- \rightleftharpoons \text{Fe}^{3+}(aq) + 3\text{H}_2\text{O} \tag{20c} \]

Magnetite:

\[ \frac{1}{2} \text{Fe}_3\text{O}_4(s) + 4\text{H}^+ + e^- \rightleftharpoons 3\text{Fe}^{2+}(aq) + 2\text{H}_2\text{O} \tag{20d} \]

The Nernst equations for all these reactions, except magnetite, are identical to the one in eq 13. The Nernst equation for the magnetite half-reaction is

\[ \text{E}_H = \text{E}^{0}_H - \frac{3RT}{2F} \ln([\text{Fe}^{3+}(aq)]) + \frac{4RT}{F} \ln([\text{H}^+]) \tag{21} \]

We previously measured the \textit{E}^{0}_H value for the hematite-Fe^{3+} half reaction (0.768 \pm 0.002 V).\textsuperscript{52} We calculated \textit{E}^{0}_H values for the half-reactions containing lepidocrocite (0.846 V), ferrihydrite (0.937 V), and magnetite (1.067 V) using existing thermodynamic data.\textsuperscript{61,62} While solutions containing lepidocrocite and ferrihydrite are not at thermodynamic equilibrium (i.e., the oxides should transform to more stable phases), the \textit{E}^{0}_H values can be useful approximations if the oxides remain stable over the course of the reaction. Values of \textit{E}_H were calculated according to Fe^{2+}(aq) activity, pH, and \textit{E}^{0}_H values (data in Tables S2 and S3). Calculated \textit{E}_H values were also corrected to account for differences of reactivities of the substituted nitrobenzene by normalizing reaction rate constants according to their \textit{E}_H values to nitrobenzene using eq 19.

All the reduction rate constants compiled from the literature for goethite, hematite, lepidocrocite, and ferrihydrite exhibited a clear linear trend consistent with the linear free energy relationship developed for goethite (Figure 5). In the case of magnetite, the data initially did not fall on the line when we

Figure 4. log(k_{obs}) values as a function of pH and the calculated \textit{E}_H value of the goethite-Fe^{2+} redox couple for data compiled from the literature.\textsuperscript{3,6,43} The method used to calculate \textit{E}_H values is provided in section S2. Reactor conditions varied between reported experiments: total Fe^{2+} ranged between 0.375 and 1.24 mM, goethite loading ranged between 0.025 and 1.54 g/L, BET specific surface areas of goethite ranged between 16.2 and 51 m\(^2\)/g, and pH values range between 6.1 and 7.97. The line shown is the fit from Figure 3.
A critical assumption implicit to this approach is that Fe(II)-oxidation results in homoeopitaxial growth of the underlying oxide (e.g., goethite grows on goethite), with the exception of magnetite. In the case of goethite, several studies have indeed found that Fe(II)-oxidation leads to goethite particle growth.37,38,43 Ferricydrite, hematite, and lepidocrocite are more complicated. In the case of hematite, Fe(II)-oxidation can lead to both the growth of hematite and the nucleation of goethite particles.38 Interestingly, this does not influence the thermodynamic calculations because the half reactions for the oxidation of Fe(II) to hematite or goethite have virtually identical $E^\circ_H$ values and identical Nernst equations.32 Very little work has examined what Fe(II)-oxidation products form in the presence of lepidocrocite or ferricydrite.8 Both oxides are known to undergo secondary mineralization reactions to more stable phases in the presence of aqueous Fe(II) at circumneutral pH values.63-67 It is therefore likely that Fe(II) may oxidize to form oxides that are different from the original phase, which could explain why the ferricydite and lepidocrocite points in Figure 5 are generally higher than those of goethite and hematite. With this caveat in mind, assuming that nitrobenzene reduction is coupled to homoeopitaxial oxide growth works from a practical perspective for all oxides except magnetite.

Two recent works have reported similar free energy relationships in which the authors plotted $\log(k_{rel})$ versus $E_H/0.059$ V values for multiple iron oxides and substituted nitrobenzene compounds at a single pH value.6,8,38,43 Two of the studies differed from the present work in that the authors measured $E_H$ values for suspensions by preparing parallel reactors. In both studies, the fitted slope values (0.168 or 0.49 ± 0.158) were significantly smaller than the one reported here (i.e., ≈1). In the study that observed a slope of 0.16, a portion of the reactors contained dissolved Si that blocked iron oxide surface sites and therefore affected calculated $k_{rel}$ values.8 In the other study, the authors speculated that measured $E_H$ values may have contained experimental artifacts, as the measurements depended on the concentrations of Fe(II) and iron oxide in a way that deviated from the Nernst equation.20 Note that data taken from both these studies fell on the trend line in Figure 5 when we calculated $E_H$ values based on the pH and Fe(II)aq activity and that the calculated values significantly differed from the measured ones in most cases. We are unsure as to why the calculated and measured $E_H$ values from these studies differed.

**Interpretation of the Slope Terms in the Free Energy Relationship.** The trends between $\log(k_{rel})$ and $E_H$ and pH (i.e., the slope terms $a$ and $b$ in eq 16) provide insights into the rate limiting step(s) in the reduction of reducible aromatic nitro groups by oxide-bound Fe(II). To interpret these trends, we briefly discuss the current state of knowledge regarding the reduction pathway of nitroaromatic compounds, using nitrobenzene as a surrogate (Scheme 1). The reduction of nitrobenzene (species 1 in Scheme 1) to aniline is initiated by a series of two proton and two electron transfer steps before nitrosobenzene (6) is formed as first measurable product through a dehydration step, which controls the rate of nitrobenzene disappearance. Since the reaction from 1 to 6 is irreversible under environmental conditions,41 we can confine the kinetic interpretation of the free energy relationship to these steps. Early studies examining the reduction of nitroaromatic compounds by oxide-bound Fe(II) observed linear correlations between $\log(k_{rel})$ and the one-electron reduction potential values of nitroaromatic compounds, $E_{1/2}^{\circ}$H.41 These

**Figure 5.** Compilation of $\log(k_{rel})$ values as a function of pH and the calculated $E_H$ values for the reduction of nitrobenzene by Fe(II) in the presence of goethite, hematite, lepidocrocite, ferricydrite, and magnetite. The solid line is the least-squares linear regression excluding the three outlier points (denoted with asterisks). The fit yielded a slope of 1.02 ± 0.03, a y-intercept of 3.42 ± 0.17, and an $r^2$ value of 0.92 ($n = 71$; 24 from this study, 47 from the literature, 3 outlier points excluded). The shaded area represents the 95% confidence band, and the dashed lines encompass the 95% prediction band. Data were taken from the references.3,5,9,6,43,60

...calculated $E_H$ values according to eq 21. This was likely due to the incorrect assumption that magnetite was the oxidation product that formed. A recent study that characterized the Fe(II)-oxidation product that formed when 4-chloro-nitrobenzene was reduced by suspensions containing magnetite and Fe(II)aq observed the formation of lepidocrocite, not magnetite, as the dominant oxidation product.38 When we calculated $E_H$ values assuming that lepidocrocite was the oxidation product, the magnetite data fell in line with the data for the other oxides (Figure 5).

Fitting all the data with a line yielded a slope of 0.76, a y-intercept of $-3.57$, and an $r^2$ value of 0.68 ($n = 74$, fit not shown). Excluding three outlier points, which are denoted with asterisks inside the markers, significantly improved the fit ($r^2 = 0.92$, $n = 71$) and yielded a slope of 1.02 ± 0.03 and a y-intercept of 3.42 ± 0.17 (line shown in Figure 5). Two of the outliers were points collected using a carbonate pH buffer, as discussed above. The third outlier point was excluded because it clearly deviated from the overall trend, although we could not identify an explanation as to why.60 The 95% prediction band (encompassed by the dashed lines in Figure 5) was approximately ±1 log unit on the y-axis, indicating that 95% of the reported $k_{rel}$ values were within an order of magnitude of the values that would be predicted by the free energy relationship. Some of the scatter among the data sets was likely due to variations in the buffer type and concentrations used in each study. Prior work found that commonly used pH buffers caused iron oxide particle aggregation, which influenced $k_{rel}$ values by up to 0.5 log units.41 This ability for the free energy relationship to describe the literature data indicates that pH values and $E_H$ values for oxide-Fe(II)aq redox couples can be used to estimate nitrobenzene, and likely nitroaromatic, transformation rate constants within an order of magnitude.
observations led to the hypothesis that the first electron transfer step to nitrobenzene, \( 1 \equiv 2 \), was a suitable descriptor of the relative reduction rates and potentially the rate-limiting step of reactions 1 to 6 (Scheme 1). \(^{41,58}\) More recent evidence from large \(^{15}\)N kinetic isotope effect associated with the reduction of substituted nitrobenzenes \(^{45-47,68}\) implied, however, that the dehydration step of the \( \text{N,N-dihydroxyaniline} \ (5 \rightarrow 6) \) was the rate-limiting step, consistent with electrochemical experiments examining the reduction of aromatic NO\(_2\) groups. \(^{69,70}\)

We examined if the free energy relationship observed here was consistent with (i) reaction 5 \( \rightarrow 6 \) being the rate-limiting step and (ii) one-electron reduction potentials being used as descriptors for variations in reduction rate constants. We derived a rate expression for the reduction of nitrobenzene by \( \text{Fe}^{2+} \), assuming that 5 \( \rightarrow 6 \) was the rate-limiting with the quasi-equilibrium method, which assumes that the preceding reaction steps are in equilibrium (the derivation is in the subsection “Derivation of Free Energy Relationship” above). \(^{30,42,55}\) This method is thought to be valid if the rate constant of the rate-limiting step is at least 100 times smaller than those of the preceding steps. \(^{42}\) With eq 11, we are able to reconcile potentially contradicting views with regard to the rate-limiting step of aromatic NO\(_2\) group reduction. Note that even though we assume that reaction 5 \( \rightarrow 6 \) is rate-limiting, \( \log(k_{\text{obs}}) \) scales linearly with changes of \( E_{\text{H}}^l/0.059 \) V in constant \( d \), as shown in the derivation.

The derived slope terms (\( a \) for the \( E_{\text{H}}/0.059 \) term and \( b \) for the \( \text{pH} \) term) in eq 11 are both \(-2\). Note that the \( b \) term does not reflect the overall \( \text{pH} \)-dependency of the reaction since the \( E_{\text{H}} \) value is itself \( \text{pH} \)-dependent. The derived equation can also be expressed in terms of equilibrium constants instead of \( E_{\text{H}} \), in which case the derived rate expression indicates that reaction kinetics would be second-order with respect to \([ \text{Fe}^{2+} ]\) and forth-order with respect to \(1/\text{[H}^+]\) (eq 5f). Clearly, the derived \( a \) and \( b \) terms differed from the observed terms, which were both \( \approx -1 \). The observed values instead indicate that the reaction rate constants depend only on the free energy changes associated with transferring one proton and one electron to nitrobenzene. There are two possible explanations for the discrepancy. The first is that the quasi-equilibrium assumption used to derive the theoretical relationship is invalid for this system because the preceding reaction steps do not reach equilibrium. Such a case can arise when rate constants have similar orders of magnitude. \(^{55}\) The second possibility is that the second electron transfer step \((3 \equiv 4)\) and second proton transfer step \((4 \equiv 5)\) in Scheme 1 have sufficiently lower activation-free energies than the preceding ones, making the steps kinetically irrelevant. In either case, this exercise demonstrates that free energy relationship for \( \log(k_{\text{obs}}) \) depends on the transfer of one proton and one electron to nitrobenzene, not two of each.

**Environmental Implications.** In this work, we observed that \( E_{\text{H}} \) values of oxide-bound \( \text{Fe}^{2+} \) could be used to accurately describe variations in nitrobenzene reduction rate constants. This finding is significant because it validates the use of thermodynamic data for oxide-bound \( \text{Fe}^{2+} \) to explain trends in nitroaromatic reduction rate constants. The data indicate that it is unnecessary to describe “adsorbed \( \text{Fe}^{2+} \)” as a discrete species when explaining trends in pollutant transformation rates. Instead, the \( E_{\text{H}} \) of \( \text{Fe}^{2+} \) which can be calculated from readily available thermodynamic data, \(^{41,62}\) can be used effectively. The extent to which this free energy relationship can be applied to other classes of pollutants containing different reducible functional groups remains unclear at this point due simply to the lack of data, but it seems highly probable that that \( E_{\text{H}} \) values will be useful if the reaction is completely or partially rate-limited by one or more electron transfer steps. Of course, in real environmental systems, pollutant reduction rates will also be affected by other species, such as carbonate, natural organic matter, and silicate, which compete for reactive sites and/or passivate iron oxide surfaces.

The findings from this work can also explain a puzzling observation. Past works found negligible reduction of nitrite, molecular oxygen, and nitrobenzene occurred when an iron oxide was exposed to \( \text{Fe}^{2+} \) and either the residual \( \text{Fe}^{2+} \) was removed or most of the \( \text{Fe}^{2+} \) was taken up the oxide. \(^{76,19,29}\) This observation was difficult to reconcile with the hypothesis that oxide-bound \( \text{Fe}^{2+} \) is a strong reductant. \(^{21}\) The observation can, however, be explained based on the observations from this study. Removing \( \text{Fe}^{2+} \) from the system makes the \( E_{\text{H}} \) values of both \( \text{Fe}^{2+} \) and oxide-bound \( \text{Fe}^{2+} \) more positive. This suggests that the concentration of \( \text{Fe}^{2+} \) in groundwater systems can be used an important predictive parameter for pollutant fate, as it is a proxy for oxide-bound \( \text{Fe}^{2+} \) \( E_{\text{H}} \) values in the presence of iron oxides.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00481.

Reaction scheme of nitrobenzene reduction steps and ferrous iron oxidation, example kinetic data of nitrobenzene reduction, and tabulated experimental and literature data (PDF)

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**Notes**

The authors declare no competing financial interest.

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