pH-Dependent Reactivity of a Water-Soluble Nickel Complex: Hydrogen Evolution vs Selective Electrochemical Hydride Generation

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ABSTRACT: Mechanistic details for the aqueous hydrogen evolution reaction (HER) electrocatalyst [Ni(DHMPE)2]2+ (DHMPE = 2-bis(bis(hydroxymethyl)phosphino)ethane) are reported. The proposed 2e− reduced catalytic intermediate [Ni(DHMPE)2]2+ was added to solutions between pH 1 and 5. The two sequential protonation events leading to H2 evolution were monitored by 31P{1H} NMR spectroscopy. The initial protonation event to generate the metal hydride [HNi(DHMPE)2]+ proceeds to completion within 1.5 min. In contrast, significant variation in the pH-dependent rate and reaction progress of the second protonation event to form the H−H bond is observed. The differences are discussed in the context of the free energy of each protonation event, which also defines the pH conditions under which H2 evolution is exergonic. The analysis provides useful information on the functional pH range of HER electrocatalysts that proceed through metal hydride intermediates. Reductive electrolysis of [Ni(DHMPE)2]2+ under conditions in which H2 evolution is endergonic (pH 7) leads to selective generation of the corresponding metal hydride [HNi(DHMPE)2]+. The electrolytic generation of a kinetically competent reducing metal hydride intermediate with minimal H2 evolution illustrates a route for accessing selective reduction of non-proton substrates.

INTRODUCTION

The electrocatalytic reduction of feedstock chemicals to fuels is an important step toward converting renewable electricity into a medium more suitable for energy storage and transportation applications. Proton reduction from water is a focal point for electrocatalytic fuel generation because hydrogen can be used directly as a fuel or as a chemical reductant. As a result, there has been robust interest in developing and understanding aqueous electrocatalysts for the hydrogen evolution reaction (HER). We recently reported the complex [Ni(DHMPE)2]2+ (DHMPE = 2-bis(bis(hydroxymethyl)phosphino)ethane) (1) (Chart 1). [Ni(DHMPE)2]2+ (1) is a robust and active electrocatalyst for proton reduction at pH 1, a common operating condition in commercial electrolyzers. Our proposed mechanism is shown in Chart 1. In water, dimethyl sulfoxide (DMSO), and acetonitrile, [Ni(DHMPE)2]2+ (1) exhibits a 2e− irreversible reduction to [Ni(DHMPE)2]2+ (2) (Chart 1). In our prior study, various acid sources were utilized in DMSO to demonstrate stepwise generation of the metal hydride [HNi(DHMPE)2]+ (3) followed by protonation to evolve H2.

In this study, we investigated the pH-dependent mechanism of aqueous hydrogen evolution. The rate and degree of completion for each protonation step are discussed in the context of its thermodynamic free energy. The results illustrate how hydricity, or the heterolytic cleavage energy of the metal hydride (3), determines the functional range for favorable H2 evolution.

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nonprotic substrates. To this end, we demonstrate the selective electrolytic generation of the metal hydride intermediate ([HNI(DHMPE)]₂⁺ (3) in Chart 1) from [Ni(DHMPE)₂]²⁺ (1) at pH 7 with little or no H₂ evolution under both aqueous conditions and DMSO.

## RESULTS AND DISCUSSION

**Metal Hydride Formation and pH-Dependent Hydrogen Evolution.** Each nickel species in the proposed catalytic cycle shown in Chart 1 has been independently synthesized and characterized. ¹⁻³ are all diamagnetic with diagnostic ³¹P NMR signatures in acetonitrile and DMSO. ¹⁻³ are all soluble in water, but ² has never been observed, as it rapidly protonates to generate ³ (vide infra). However, ² can be synthesized in tetrahydrofuran or CH₃CN and isolated as a solid. ³¹P{¹H} NMR spectroscopy was used to directly monitor the two sequential protonation reactions upon dissolution of ² in water to first generate the metal hydride (³) and then evolve H₂ to regenerate the resting state catalyst (¹).

The reduced complex [Ni(DHMPE)₂]⁻ (2) was added to aqueous buffered solutions between pH 1 and 5. The solutions consist of a 10-fold excess of buffer so that proton activity does not change significantly over the course of the experiment.

The first ³¹P{¹H} NMR spectrum was taken at 1.5 min and every 2.5 min thereafter for 75 min. The first protonation to generate [HNI(DHMPE)]⁺ (3) (singlet at 54 ppm) is rapid at all pH values and the initial Ni(0) species (²) is never observed under these conditions. The spectra over 75 min at pH 2.5 are shown in Figure 1; compiled spectra for all other pH values are shown in Figures S1–S8.

**Figure 1.** ³¹P{¹H} NMR spectra displaying protonation of [HNI(DHMPE)]⁺ (3) (singlet at 54 ppm) to release H₂ and generate [Ni(DHMPE)]²⁺ (1) (singlet at 65 ppm) at pH 2.5 over time (spectra were recorded every 2.5 min for 75 min, from bottom to top). Time-resolved spectra between pH 1 and 5 are shown in Figures S1–S8.

The second protonation event with the metal hydride (³) results in H–H bond formation and generation of the four-coordinate Ni(II) species [Ni(DHMPE)₂]²⁺ (1) (singlet at 65 ppm). The ³¹P{¹H} NMR spectra contained an internal standard to confirm the total amount of nickel hydride complex (³) and Ni(II) complex (¹) is conserved (there are no decomposition or off-cycle reaction pathways).

Figure 2 shows the concentrations of ³ (dashed) and ¹ (solid) over 75 min, color coded by pH. At pH 1, both protonation events occur within 4 min. Between pH 1.5 and 5, protonation occurs more slowly before the concentrations of ³ and ¹ approach stable values. The reaction progress (K) is described by the relative concentrations of the resting state (¹) after H₂ evolution and the nickel hydride (³) (or [¹]/[³]). After 75 min, the reaction progress (K) for protonation of the metal hydride (³) to evolve H₂ ranges from ~27 to 10⁻² for this reaction from pH 1.5 through 4.5 (see Table 1). K declines with increasing pH values. Above pH 3 the reaction proceeds to less than 50% completion after 75 min. At pH 5 no protonation is observed after 75 min—only the metal hydride (³) is found in solution.

**Kinetics of Protonation.** The first protonation step to generate nickel hydride (³) is rapid and is never observed between pH 1 and 5. We were unable to discern quantitative rates for the formation of ³ using electrochemical techniques because of the nonideal irreversible 2e⁻ reduction of ¹ in the cyclic voltammogram. However, we note that rates of protonation to generate cobalt and nickel hydride complexes have been reported using systems that were more ideally suited for kinetic studies.⁶

In contrast to the first protonation event, the second protonation event is observed at all pH values, indicating that the latter is slower. In aqueous solutions, electrochemical reduction of ¹ is under diffusion control, indicating that electron transfer is rapid.³⁵ Thus, protonation of the metal hydride to form the H–H bond is likely the rate-determining step during catalysis.

Analysis of the initial rate between pH 1.5 and 4.5 indicates a first-order reaction with respect to proton concentration (see Figure S9). An initial rate constant (k₁₀₀) was determined at each pH, and the values are given in Table S1. Protonation occurs very rapidly at the low pH values, limiting the data available for kinetic analysis. At pH 1, only one spectrum is obtained before the reaction is complete; therefore, the calculated observed rate represents a lower bound. No protonation of the metal hydride (³) is observed at pH 5 after 75 min. The relationship between log k₁₀₀ for H₂ evolution and pH is shown in Figure 3.

**Thermodynamic Considerations of Metal Hydride Formation and Hydrogen Evolution.** The pH-dependent reaction progress given in Table 1 and kinetic relationships (Figure 3) can be contextualized with regard to the free energy of the protonation reactions. The free energies of the first and second protonation steps are dependent on the pHKᵣ and hydricity, respectively, of the metal hydride. The pHKᵣ value of [HNI(DHMPE)]⁺ is ≥15 in water.⁵ The first protonation step in Chart 1 is exergonic under all of the conditions we examined (pH 1–5).

The free energy of the second protonation to evolve hydrogen (eq 4 in Scheme 1) is dictated by the hydricity of the metal hydride (eq 1), the proton activity (or pH) of the reaction conditions (eq 2), and the solvent-dependent heterolytic bond cleavage energy of H₂ (eq 3). This relationship is depicted at the bottom of Scheme 1. The hydricity of [HNI(DHMPE)]⁺ was measured to be 30.0 kcal/mol in water¹ and is represented by the dashed red line in Scheme 1. The calculated ΔG values for H₂ evolution under the standard state conditions of 1 atm of H₂ for each pH condition of our study are shown in Table 1. From this analysis, we see that protonation to evolve H₂ is thermoneutral.
at pH 3.1 (i.e., $pK_{a2} = 3.1$). H$_2$ evolution is exergonic at lower pH values and endergonic above it.

The standard state for eq 4 (Scheme 1) is 1 atm of H$_2$. Our NMR experiments were carried out under 1 atm of N$_2$ instead of 1 atm of H$_2$ to replicate conditions used in catalytic hydrogen production. Despite the change in atmosphere, we find reaction progress after 75 min, at which point the concentration of H$_3$ and 1 is only minimally changing, is consistent with the free energy calculated for the reaction.

![Figure 2. Concentration of $[\text{HNi(DHMPE)}_2]^+$ (3) (left, solid lines with squares) and $[\text{Ni(DHMPE)}_2]^{2+}$ (1) (right, dashed lines with triangles) after dissolution of Ni(DHMPE)$_2$ (2) in aqueous solutions between pH 1 and 5, recorded every 2.5 min over 75 min. Concentrations were measured by normalizing the integrated $^{31}$P{H} NMR peaks of each species; comparison to a capillary integration standard confirms quantitative conversion from 3 to 1.](image)

![Figure 3. $\log k_{obs}$ vs pH for H$_2$ formation at pH 1−5 on the basis of $^{31}$P NMR spectroscopic data. The $k_{obs}$ value at pH 1 represents a lower bound (see main text).](image)

The pH-dependent free energy of protonation to deliver H$_2$ also provides insight into the observed rate. The plot of $\log k_{obs}$ vs pH illustrates a decline in rate that correlates with the free energy of the reaction. A linear free energy relationship with proton activity has previously been observed with nickel and cobalt hydrides under conditions in which H$_2$ evolution is exergonic.

When the free energy of protonation becomes positive, the ratio [1]/[3] falls below 1 as expected. Additionally, the extent to which the reaction proceeds decreases about 1 order of magnitude per increase in pH unit, which is consistent with the change in free energy.

$\Delta G^o_{\text{obs}}$ (kcal/mol) for H$_2$ formation by heterocoupling (or protonation) of a metal hydride intermediate and (bottom) thermochemistry of metal hydride protonation (eq 4) by hydricity and pH used to determine $pK_{a2}$.

![Scheme 1. (Top) Thermodynamic Cycle Describing H$_2$ Formation by Heterocoupling (or Protonation) of a Metal Hydride Intermediate and (Bottom) Thermochemistry of Metal Hydride Protonation (Eq 4) by Hydricity and pH Used to Determine $pK_{a2}$](image)
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... decreases as the thermodynamic driving force for \( \text{H}_2 \) formation decreases, with an apparent inflection around where protonation is thermoneutral \((\Delta G = 0)\).

We attempted to measure rates of electrocatalytic \( \text{H}_2 \) evolution at higher pH values. However, lower proton activities require high scan rates to achieve pure kinetic conditions, at which point we observe diffusion-controlled processes from \([\text{Ni(DHMPE)}]^{2+}\) reduction due to slowing catalytic rates. Nevertheless, our kinetic data for the rate-determining step indicate that the rate of \( \text{H}_2 \) evolution decreases with increasing pH.

Selective Electrolytic Generation of Metal Hydride. Under Aqueous Conditions. Transition-metal hydrides are also important intermediates in a broad range of reduction reactions.\(^8\) Metal hydride intermediates for reduction chemistry are most commonly accessed using hydrogen and a base or a hydride donor. Performing these reductions through electrolysis would minimize the use of sacrificial reductants by generating metal hydride using electrons from an electrode and protons from solution. However, parasitic \( \text{H}_2 \) evolution in solutions that contain protons can undermine Faradaic efficiency or product yield in comparison to total current passed and presents a major challenge in reductive electrolysis.\(^9\)

The thermodynamic analysis described above also provides valuable information on how to suppress \( \text{H}_2 \) evolution while maintaining sufficient proton activity to generate a metal hydride. This information provides an entry point to achieving selective reduction of non-proton substrates, an approach that has been successful for both heterogeneous\(^2\) and homogeneous catalysts.\(^1\)

Controlled-potential electrolysis of \([\text{Ni(DHMPE)}]^{2+}\) was performed under various conditions to demonstrate isolation of the corresponding hydride after aqueous electrolysis (electrolysis cell is shown in Figure S10). In all of the controlled-potential electrolysis experiments (under \( \text{H}_2 \) or \( \text{N}_2 \)), the products were quantified against an internal standard by \( ^{31}\text{P} \{^1\text{H} \} \text{NMR} \) to ensure that the total amount of nickel complex was conserved (no degradation was observed in the postelectrolysis solutions). We demonstrated in our prior study that no changes in electrolytic behavior occur upon addition of elemental mercury, and no residual compound was observed after rinsing the electrode.\(^3\) Both experiments indicate that these nickel complexes are not prone to decomposition or, at absorption onto the electrode. We also previously determined that the nickel hydride (2) is stable with respect to homolytic \( \text{H}_2 \) evolution.\(^3\)

An electrolysis of 1 was performed under 1 atm \( \text{H}_2 \) in a pH 7 buffered (glycinamide) solution of \([\text{Ni(DHMPE)}]^{2+}\) (Figure S11; at this pH, \( \Delta G \) value of \( \text{H}_2 \) evolution is 5.3 kcal/mol according to eq 4 in Scheme 1). Upon electrolysis at \(-0.8\) V vs SHE (about 270 mV beyond the two-electron reduction potential of \([\text{Ni(DHMPE)}]^{2+}\) and passing of a little more than 2 equiv of charge, \([\text{HNi(DHMPE)}]^{+}\) (3) is the only species observed in solution (Figure 4, middle). We note that this electrolysis was performed under 1 atm of \( \text{H}_2 \) to be consistent with the thermodynamics of protonation described in eq 4. While performing electrolysis under 1 atm of \( \text{H}_2 \) may be practical for achieving selective reduction for products that remain in solution, it is less desirable for reactions that produce gaseous products.

Therefore, we repeated the electrolysis of 1 under the same conditions (pH 7) except under 1 atm of \( \text{N}_2 \) (Figure S12).

![Figure 4. \( ^{31}\text{P} \{^1\text{H} \} \text{NMR} \) spectra of \([\text{Ni(DHMPE)}]^{2+}\) (1) before (blue, top) and after electrolysis at \(-0.8\) V vs SHE at pH 7 for 7 h under 1 atm of \( \text{H}_2 \) (green, middle) and 1 atm of \( \text{N}_2 \) (red, bottom).](image)

After a similar amount of charge was passed, \([\text{HNi(DHMPE)}]^{+}\) and \([\text{Ni(DHMPE)}]^{2+}\) were both present in the postelectrolysis solution in a nearly 7/1 ratio (Figure 4, bottom). Additionally, when the sealed headspace of the electrolysis was analyzed, only \(~0.6\) equiv of hydrogen (with respect to nickel) was detected. Although operation under a non-\( \text{H}_2 \) atmosphere leads to some protonation of the hydride to form \( \text{H}_2 \), a high concentration of \([\text{HNi(DHMPE)}]^{+}\) was still isolable after electrolysis. This result demonstrates that \([\text{HNi(DHMPE)}]^{+}\) can be generated as a kinetically competent intermediate under electrolytic conditions.

In Dimethyl Sulfoxide (DMSO). Although all of the conditions described thus far have focused on aqueous catalysis, the thermodynamic cycle in Scheme 1 is also applicable to other solvent systems, provided the appropriate hydricity (eq 1), \( \text{pK}_a \) scale (eq 2), and heterolytic bond cleavage energy of \( \text{H}_2 \) (eq 3) for that solvent is used. Since the thermodynamic properties of \([\text{HNi(DHMPE)}]^{+}\) (3) in DMSO have been measured, we utilized the data to determine conditions for selective electrochemical generation.

In DMSO the hydricity of 3 is 55.5 kcal/mol and the \( \text{pK}_a \) is 9.26.\(^6\) Using the heterolytic bond cleavage energy of \( \text{H}_2 \) (60.7 kcal/mol in DMSO), the \( \text{pK}_a \) value where hydrogen evolution is thermoneutral (from Scheme 1) is calculated to be 3.8. Therefore, tri-\( n \)-butylammonium ([\( \text{HNBu}_3 \] \)]\(^+\), \( \text{pK}_a = 8.4 \) in DMSO)\(^13\) is sufficiently acidic to generate 3 from the reduced complex 2 without resulting in significant protonation of 3 to form \( \text{H}_2 \). After a solution of \([\text{Ni(DHMPE)}]^{2+}\) underwent controlled-potential electrolysis at \(-2.0\) V vs Fe(\( \text{C}_2 \text{H}_5 \))\(^2+/0\) (Figure S13) in the presence of 10 equiv of \([\text{HNBu}_3 \] \)]\(^+\) under an \( \text{N}_2 \) atmosphere, only \([\text{HNi(DHMPE)}]^{+}\) was observed in the postelectrolysis \( ^{31}\text{P} \{^1\text{H} \} \text{NMR} \) spectrum (Figure S14).

**CONCLUSION**

The hydrogen evolution activity of electrocatalyst \([\text{Ni(DHMPE)}]^{2+}\) (1) was previously described at pH 1. This study investigated the pH-dependent reactivity of the 2e” reduced proposed intermediate \([\text{Ni(DHMPE)}]^{2+}\) (2) using \( ^{31}\text{P} \{^1\text{H} \} \text{NMR} \) spectroscopy. Dissolution of 2 in aqueous solutions between pH 1 and 5 permits investigation into both protonation reactions prior to \( \text{H}_2 \) evolution. The first
protonation to generate the metal hydride \([\text{HNi(DHMPE)}_2]^+\) (3) rapidly proceeds to completion in this pH range, and 2 is never observed. The rate and extent of protonation of the metal hydride to evolve \(\text{H}_2\) at each pH was correlated to the free energy of that reaction, which can be calculated using the hydricity of 3.

Conversely, the hydricity can also be utilized to determine conditions under which the metal hydride \([\text{HNi(DHMPE)}_2]^+\) (3) in water and DMSO. We believe this type of analysis provides a possible route to accessing metal hydride intermediates for reactivity and reductive catalysis. We believe these quantitative studies are valuable to advancing our understanding of metal hydride reactivity and reductive catalysis.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00558.

Experimental details, NMR data, controlled-potential electrolysies, and pre- and post-electrolysis analyses (PDF)

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Notes
The authors declare no competing financial interest.

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