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Direct Determination of Equilibrium Potentials for Hydrogen Oxidation/Production by Open Circuit Potential Measurements in Acetonitrile

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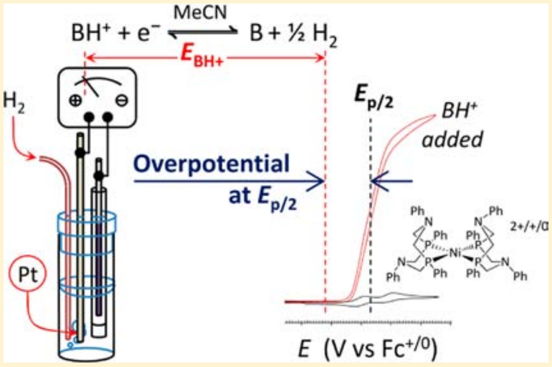
Ⓢ *Supporting Information*

ABSTRACT: Open circuit potentials were measured for acetonitrile solutions of a variety of acids and their conjugate bases under 1 atm H_2. Acids examined were triethylammonium, dimethylformamidium, 2,6-dichloroanilinium, 4-cyanoanilinium, 4-bromoanilinium, and 4-anisidinium salts. These potentials, along with the pK_a values of the acids, establish the value of the standard hydrogen electrode (SHE) potential in acetonitrile as −0.028(4) V vs the ferrocenium/ferrocene couple. Dimethylformamidium forms homoconjugates and other aggregates with dimethylformamide; open circuit potentials (OCPs) were used to quantify the extent of these reactions. Overpotentials for electrocatalytic hydrogen production and oxidation were determined from open circuit potentials and voltammograms of acidic or basic catalyst solutions under H_2. For these solutions, agreement between OCP values and potentials calculated using the Nernst equation is within 12 mV. Use of the measured equilibrium potential allows direct comparison of catalytic systems in different media; it requires neither pK_a values, homoconjugation constants, nor the SHE potential.



INTRODUCTION

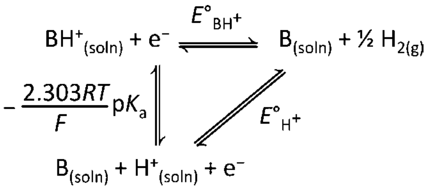
Research toward sustainable, cost-effective energy technologies is focused on the interconversion of electrical and chemical energy. Catalysts for this interconversion are characterized by the relationship between the rate of catalysis, indicated by an increased current on adding a catalytic substrate, and the overpotential, defined as the difference between the potential of an electrode mediating a given half-reaction and the equilibrium potential for that half-reaction.[1] The simplest reaction of this kind interconverts a Brønsted acid with hydrogen and the corresponding base (eq 1); E_{BH^+} is its equilibrium (thermodynamic) potential.

$$BH^+_{(soln)} + e^- \overset{E_{BH^+}}{\rightleftharpoons} B_{(soln)} + \frac{1}{2}H_{2(g)} \qquad (1)$$

The cyclic voltammograms in Figure 1 show a molecular electrocatalyst with no added acid and a larger sigmoidal wave obtained on adding acid, indicating reduction of protons to produce hydrogen. This response represents "pure kinetic" conditions as described by Savéant,[1] wherein the maximum current depends on the rates of chemical steps proceeding at steady state, i.e. with rates that do not vary with time. At a potential of $E_{p/2}$ the catalytic current is at half its maximum value; the overpotential at $E_{p/2}$ (the difference between E_{BH^+} and $E_{p/2}$) is characteristic of the catalyst under the conditions employed. For electrocatalyst systems exhibiting kinetic control, the comparison of $E_{p/2}$ with E_{BH^+} is apt since a "perfect" catalyst operating under steady-state conditions will afford a wave with zero overpotential, i.e., a half-peak potential coincident with the equilibrium potential E_{BH^+}.[2] A sigmoidal response is not always obtained in these catalytic reactions; however, provided the current increases rapidly over a limited potential range, estimates of the half-peak potential $E_{p/2}$ may be obtained from this data by various methods.[3] The problem of determining E_{BH^+} is more difficult and thus contributes substantially to the uncertainty in determining overpotentials.

The standard-state potential $E^\circ_{BH^+}$ for reaction 1 may be computed according to Scheme 1 with water or acetonitrile, as those solvents have both a pK_a scale and a value for the potential $E^\circ_{H^+}$ of the standard hydrogen electrode (SHE).

Scheme 1. Thermochemical Cycle Relating $E^\circ_{BH^+}$ with pK_a and $E^\circ_{H^+}$



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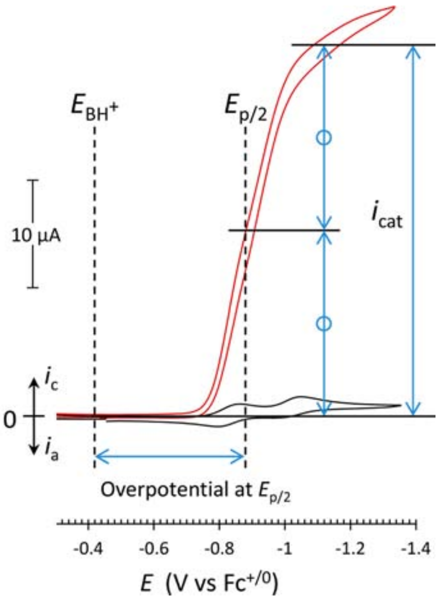
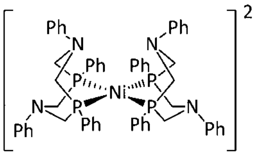


Figure 1. Cyclic voltammograms of $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$ in acetonitrile ($^nBu_4N^+PF_6^-$) under H_2 (1 atm, black trace) with 1:1 $[(DMF)H]^+OTf^-$:DMF (0.40 M, red trace), collected with $\upsilon = 0.1$ V s^{-1}. Fc$^{+/0}$ is the half-wave potential of the ferrocenium/ferrocene redox couple. The value of i_{cat} was selected as described in ref 3b. $E_{p/2}$ denotes the half-peak potential of the catalytic wave. E_{BH^+} denotes the equilibrium potential for reaction 1.



$[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2]^{2+}$

The potential E_{BH^+} is related to the standard state potential $E^\circ_{BH^+}$ by the Nernst equation (eq 2), where $Q = \alpha_B \alpha_{H_2}{}^{1/2}/\alpha_{BH^+}$.

$$E_{BH^+} = E^\circ_{BH^+} - \frac{2.303RT}{F}\log(Q) \tag{2}$$

A robust pK_a scale spanning more than 28 units exists for acetonitrile.[4] However, published values[3a,5] of $E^\circ_{H^+}$ range from −0.034 to −0.26 V vs Fc$^{+/0}$ (the formal potential of the ferrocenium/ferrocene redox couple). As more efficient (lower overpotential) catalyst systems are reported, this 230 mV uncertainty (5.2 kcal mol^{-1} at 25 °C) becomes increasingly significant.[3a] Moreover, computing E_{BH^+} using eq 2 and assuming that the analytical concentrations of acid and base are equal to their activities introduces errors in cases where acid and base molecules aggregate, as with homoconjugation. These effects are more pronounced at high substrate concentrations, which are often required to obtain steady state kinetics in electrocatalytic production or oxidation of hydrogen.

The open circuit potential (OCP) is a fundamental property of any electrochemical cell. In 1965, Kolthoff and Thomas used OCP values to determine E_{BH^+} vs a AgCl/Ag reference electrode for acetonitrile solutions containing sulfuric acid, bisulfate, and hydrogen.[5c] OCP measurements have also been used to determine E_{BH^+} in water[6] and in several protic ionic liquids.[7] As we demonstrate here, E_{BH^+} may be determined by OCP measurements for a number of different acid-base systems in acetonitrile. In conjunction with catalytic studies performed under the same conditions, directly measured values of E_{BH^+} permit the straightforward and precise determination of overpotentials.

Our results reported here also lead to a revised value for the SHE in acetontrile: using data from four different acid−base systems in acetonitrile and extrapolating to infinite dilution, we have calculated $E^\circ_{H^+}$ by the thermochemical cycle shown in Scheme 1. The consistency among these results and the observed adherence to eq 2 demonstrate that the OCP is the equilibrium potential for reaction 1. The OCP measurement may also be used to obtain equilibrium constants for acid−base aggregation reactions, the reversible formation of solution species by interaction of either an acid or a base with one or more other molecules. We have extracted aggregation equilibrium constants for $[(DMF)H]^+OTf^-$ in acetonitrile and have used these to calculate E_{BH^+}.

Comparison between values of E_{BH^+} obtained by OCP measurements and via the Nernst equation illustrates that either method affords a reliable basis for overpotential determination. However, reliable inputs to the Nernst equation are not universally available, and improving catalyst performance and understanding catalyst−medium interactions may involve a departure from well-characterized media. For example, we recently reported a system consisting of a catalyst dissolved in acidic ionic liquid−water mixtures of varying water content, for which no estimates of pK_a or $E^\circ_{H^+}$ were available.[8] We therefore determined the equilibrium potentials E_{BH^+} for these mixtures by OCP measurements. Directly measuring E_{BH^+} obviates the need for the assumptions inherent in calculating E_{BH^+}, requires neither an estimate of $E^\circ_{H^+}$ nor a pK_a scale, and permits comparison of catalysts operating in different solvents, with different acid−base systems, on a strictly equal footing.

■ RESULTS

Platinum metal catalyzes both the oxidation and production of H_2 (reaction 1) in a variety of media with a wide range of acid−base systems.[9] This reaction is presented as involving one cationic acid "BH^+" and one neutral base "B," but the methods presented here also apply to other acid−base systems, such as those consisting of neutral acids and anionic bases. Examining OCP values as a function of acid and base concentrations for a variety of acid−base systems in acetonitrile verifies that, at open circuit, the potential of the platinum electrode is the equilibrium potential of reaction 1.

First we describe the OCP measurement and factors influencing reproducibility and establish that the [acid]:[base] ratio influences the OCP as predicted by eq 2. We then report the results of three types of studies: (1) We examine how the OCP of 1:1 [acid]:[base] mixtures varies with concentration. By extrapolating to infinite dilution using acids of known pK_a, we obtain an estimate of $E^\circ_{H^+}$ for acetonitrile (Scheme 1). The acid−base systems examined in these studies are $[(DMF)H]^+OTf^-$:DMF, $Et_3NH^+BF_4^-$:Et_3N, and four aryl-substituted anilinium:aniline systems, all of which have been used as substrates for hydrogen production/oxidation in acetonitrile solution.[3b,10] (2) We determine overpotentials at $E_{p/2}$ for catalytic systems by voltammetry and OCP measurements, using solutions of the same composition for both measurements. This is the most precise method for anchoring overpotential scales. (3) We examine OCP values of Et_3N solutions under hydrogen but without an explicitly added acid and of $[(DMF)H]^+OTf^-$ solutions under hydrogen but without any added base. These studies permit evaluation of overpotentials for some published catalyst systems.[3b,10]

OCP Measurement. A schematic outlining the measurement is shown in Figure 2. The analyte is an acetonitrile solution of acid, base, supporting electrolyte, and a reference compound (ferrocene, Fc, or permethylferrocene, Fc*), sparged with hydrogen. A cyclic voltammogram spanning the reference couple is recorded using the glassy carbon working electrode, the pseudoreference electrode, and the counter-electrode. The OCP between the pseudoreference and platinum wire electrodes is then measured. These measurements afford the OCP vs Fc$^{+/0}$, thereby canceling the unknown junction potential[5c,11] across the membrane separating the analyte and reference compartments. This also places the OCP on the scale employed for catalysis studies and recommended by IUPAC for electrochemical studies in acetonitrile.[12] A representative OCP trace appears in Figure 3.

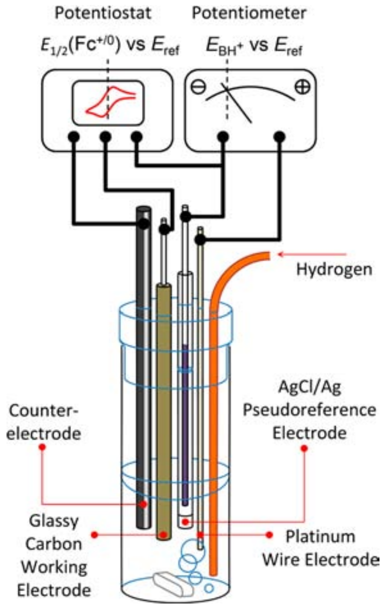


Figure 2. Schematic of the four-electrode cell configuration used for open circuit potential (OCP) measurements. The analyte solution consists of an acid:base:hydrogen mixture of known composition with an added internal reference compound such as ferrocene. Potentiostat and potentiometer are shown as separate devices to illustrate the principle of the measurement.

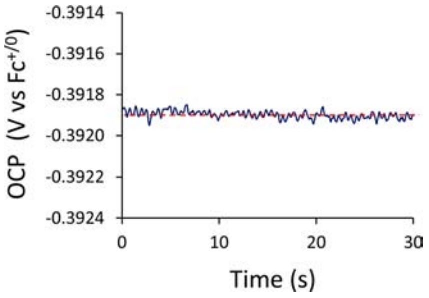


Figure 3. OCP trace showing a range of 1.0 mV. Analyte: 0.020 M [(DMF)H]$^+$OTf$^-$, 0.020 M DMF, 1.0 atm H_2, in acetonitrile (0.5 M ^{n}Bu$_4$N$^+$PF$_6^-$).

Conditioning of the platinum electrodes is the most significant factor in obtaining reproducibility. Understanding of the electrochemistry of hydrogen at polycrystalline and single-crystal platinum surfaces was significantly improved following the implementation of flame annealing as a method of pretreatment,[13] and we have found this practice to be indispensible. Platinum electrodes were immersed in fresh aqua regia, rinsed, heated in a hydrogen-air flame, cooled under hydrogen, and then handled under N_2. We used lengths of platinum wire and found that they may be reconditioned repeatedly. Conditioning requires corrosive conditions and high temperatures, so commercially available glass- or plastic-encased electrodes cannot be used. Deterioration of the electrode performance, as indicated by systematic drift or sudden large changes in the measured potential or increased signal noise, was diagnosed by replacement with a fresh electrode. Reversible waves were observed in potential sweep experiments on unstirred solutions. However, OCP rather than voltammetric measurements were chosen to avoid decomposition of MeCN at positive potentials.[13]

Selection of an appropriate reference couple depends on the redox properties of the other constituent species. For example, triethylamine and 4-anisidine are oxidized irreversibly near the Fc$^{+/0}$ potential, so we used permethylferrocene (Fc*, $E_{1/2}$ = −0.503 V vs Fc$^{+/0}$) instead in these cases. The reference compound should be introduced in a redox state that is stable at the open circuit potential: if redox occurs at E_{BH^+}, the platinum electrode will mediate this process until equilibrium is reestablished, and the solution acid:base ratio will have changed as a result. The most anodic OCP value measured in these studies was −0.220 V vs Fc$^{+/0}$, with 0.40 M [(DMF)H]$^+$OTf$^-$. An electrode at this potential is sufficiently oxidizing to convert only 0.02% of the ferrocene to ferrocenium. Reference compound concentrations were generally less than 1 mM for all experiments.

OCP as a Function of [Acid]:[Base]. Equimolar stock solutions of the acid and base were prepared for each acid studied. Two sets of OCP data were collected, the first with aliquots of the acid added to the base, affording solutions with [acid]:[base] varying from 0.1 to 1 and the second with aliquots of base solution added to the acid. A representative data set, collected with the acid 4-bromoanilinium tetrafluoroborate (4-BrC$_6$H$_4$NH$_3^+$BF$_4^-$, pK_a = 9.43 in acetonitrile,[4a] 0.50 M stock acid and base solutions), is shown in Figure 4.

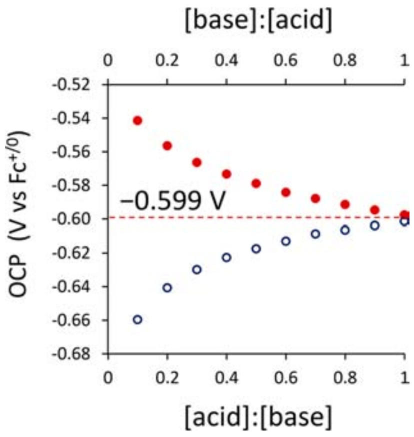


Figure 4. OCP values as a function of [base]:[acid], and of [acid]:[base], in acetonitrile (^{n}Bu$_4$N$^+$PF$_6^-$, constant total ionic strength of 0.5 M). For the data shown in filled red circles, 0.10 mL aliquots of a 0.10 M stock solution of 4-BrC$_6$H$_4$NH$_2$ in acetonitrile (0.10 M ^{n}Bu$_4$N$^+$PF$_6^-$) were added to 1.00 mL of a 0.10 M solution of 4-BrC$_6$H$_4$NH$_3^+$BF$_4^-$ in acetonitrile; for the data shown in open blue circles, aliquots of the acid solution were added to the base solution.

The OCP values converge as equimolarity is approached from either the acid-rich or base-rich solutions. These OCP data, plotted vs log([base]/[acid]), along with data using 4-cyanoanilinium tetrafluoroborate ($4\text{-}NCC_6H_4NH_3^+BF_4^-$, p$K_a$ = 7.0, 0.040 M stock solutions),[14] are shown in Figure 5. Linear fits to these plots have intercepts equal to the OCP values predicted by eq 2 with $Q = 1$. Slopes of $-2.303RT = -0.0591$ V per decade at 25 °C indicate that the assumption log([base]/[acid]) = log(Q) holds; i.e. that acid−base aggregation equilibria are not significant.

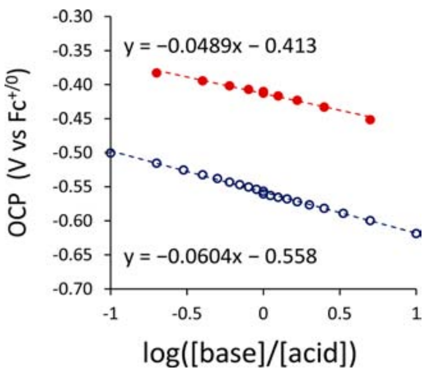


Figure 5. OCP as a function of log([base]/[acid]) for acids $4\text{-}NCC_6H_4NH_3^+BF_4^-$ (filled red circles) and $4\text{-}BrC_6H_4NH_3^+BF_4^-$ (open blue circles) in acetonitrile ($^nBu_4N^+PF_6^-$, constant total ionic strength of 0.5 M), collected under 1.0 atm hydrogen.

Slopes near −0.0591 V per decade were also obtained for $Et_3NH^+BF_4^-$ at three different stock solution concentrations (Supporting Information Figure S1); however, data collected using $[(DMF)H]^+OTf^-$ (Supporting Information Figure S2) showed a sigmoidal dependence of the OCP value on log([base]/[acid]), suggesting that in this case, aggregation is significant. Aggregation phenomena are examined in more detail below.

OCP Values as a Function of Concentration with [Acid]:[Base] = 1:1. In order to estimate equilibrium potentials in the limit of infinite dilution, we measured OCP values for a variety of 1:1 acid−base mixtures under 1.0 atm hydrogen with concentrations ranging from 0.032 mM to 0.50 M. The ionic strength was maintained at 0.5 M by diluting with acetonitrile (0.5 M $^nBu_4N^+PF_6^-$). The acids studied were $[(DMF)H]^+OTf^-$ (pK_a = 6.1),[15] 2,6-dichloroanilinium tetrafluoroborate ($2,6\text{-}Cl_2C_6H_3NH_3^+BF_4^-$, p$K_a$ = 5.06),[4a] 4-anisidinium tetrafluoroborate ($4\text{-}MeOC_6H_4NH_3^+BF_4^-$, p$K_a$ = 11.86),[4a] and triethylammonium tetrafluoroborate ($Et_3NH^+BF_4^-$, pK_a = 18.82).[4a] The acetonitrile used for these experiments was purified by passage through alumina, distillation from H_2SO_4, and then fractional distillation from CaH_2.[16] The influence of solvent impurities on the OCP response is discussed in detail in the Supporting Information; data showing these effects are presented in Figure S3. Adherence to eq 2 was obtained with concentrations ranging from 0.50 M to 4.0 mM; OCP values obtained with [acid] = [base] = 4.0 mM were taken as estimates for the OCP at infinite dilution. Table 1 presents these OCP values, the pK_a values of the acids used, and the resulting estimates of $E^\circ_{H^+}$ for acetonitrile ($^nBu_4N^+PF_6^-$) according to Scheme 1.

Table 1. OCP Values with [Acid] = [Base] = 4.0 mM for 1:1 Mixtures of Cationic Acids with Their Conjugate Bases in Acetonitrile[a]

acid	pK_a	$-RT$ ln(K_a)	OCP (V vs $Fc^{+/0}$)	$E^\circ_{H^+}$ (V vs $Fc^{+/0}$)
$2,6\text{-}Cl_2C_6H_3NH_3^+BF_4^-$	5.06	−0.299	−0.317	−0.023
$[(DMF)H]^+OTf^-$	6.1	−0.361	−0.386	−0.025
$4\text{-}MeOC_6H_4NH_3^+BF_4^-$	11.86	−0.701	−0.731	−0.032
$Et_3NH^+BF_4^-$	18.82	−1.113	−1.143	−0.031
			average	**−0.028**
			standard deviation	−0.004

[a] Estimates of $E^\circ_{H^+}$. Distilled from H_2SO_4, then from CaH_2; see ref 16b.

Interactions between acidic and basic solution species to form aggregates can influence equilibrium potentials for reaction 1 by changing the activities of participant species; the significance of this in the context of overpotential determination has been noted.[3a] Aggregation depends sensitively on the both the solvent and the structure and acid/base chemistry of the solutes.[17] Reported equilibrium constants for the 1:1 aggregation of an acid with its conjugate base (homoconjugation, eq 3) in acetonitrile solution range from $K_{B_2H} = 0\text{–}35\ M^{-1}$ for aromatic and aliphatic ammonium

$$BH^+ + B \xrightleftharpoons{K_{B_2H}} B_2H^+ \tag{3}$$

acids in acetonitrile[18] and are somewhat larger for pyridines (up to $2.7 \times 10^2\ M^{-1}$).[19] Values of K_{B_2H} can be quite large for the strong mineral acids ($6.7 \times 10^2\text{–}4.7 \times 10^3\ M^{-1}$),[20] and the carboxylic acids, sulfonic acids, and phenols ($2.0\ M^{-1}\text{–}6.3 \times 10^5\ M^{-1}$).[17a,21] Triethylamine and several anilines are reported not to undergo homoconjugation.[15,16,17a,19] Homoconjugation of $[(DMF)H]^+OTf^-$ in acetonitrile, to our knowledge, has not been previously documented.

Plots of OCP vs log([base]/[acid]) for $[(DMF)H]^+OTf^-$ (Figure 6) show a sigmoidal dependence similar to responses observed by Coetzee in potentiometric titrations of nitrogen bases.[18] This dependence is reproduced by a regression model accounting for homoconjugation (details are supplied in the Supporting Information). According to this model, the sigmoidal character should be more pronounced for higher analyte concentrations, as observed experimentally. The resulting fits to experimental data are shown in Figure 6. Refinement vs

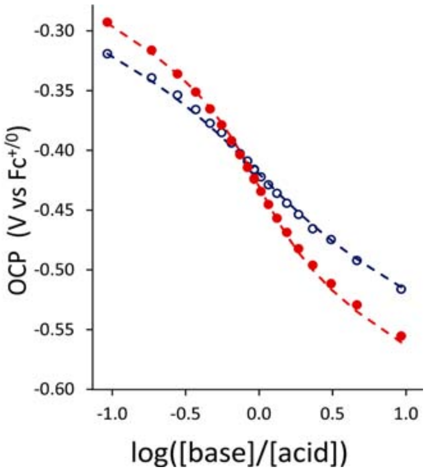


Figure 6. OCP as a function of log([base]/[acid]) for acid $[(DMF)H]^+OTf^-$ and base DMF in acetonitrile ($^nBu_4N^+PF_6^-$, constant total ionic strength of 0.5 M), collected under 1.0 atm hydrogen. Molar ratios were adjusted as described in Figure 4. Acid and base stock solutions were 0.50 M (filled red circles) or 0.10 M (solid blue circles). Fits to experimental data (dashed lines) use the homoconjugation model described in the Supporting Information.

experimental data using the homoconjugation model afforded an estimate of K_{B_2H} = 49 M^{-1}.

OCP values of 1:1 $[(DMF)H]^+OTf^-$:DMF mixtures depend strongly on the total analyte concentration. Equation 3 alone does not account for this dependence: the degree of homoconjugation does not affect the ratio α_B/α_{BH^+}, since formation of the homoconjugate B_2H^+ sequesters one equiv each of BH^+ and B. Therefore, the OCP value should not vary with analyte concentration. The dependence observed with $[(DMF)H]^+OTf^-$ (Figure 7) indicates a larger value of α_B/α_{BH^+} at higher concentrations, implying an aggregation reaction that involves more BH^+ than B.

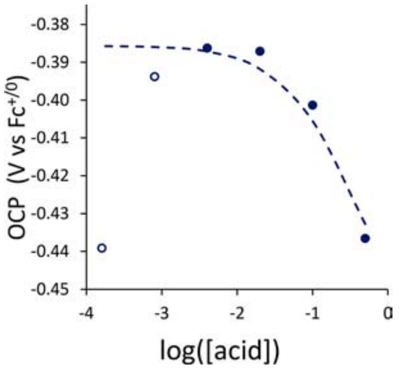


Figure 7. OCP values as a function of log([acid]), equal to log([base]), in acetonitrile ($^{n}Bu_4N^+PF_6^-$; ionic strength of 0.5); acid:base = 1:1 $[(DMF)H]^+OTf^-$:DMF. Data from the two most dilute solutions (open circles) was not employed in the determination of aggregation equilibrium constants. Acetonitrile was distilled first from H_2SO_4, then from CaH_2. The fit to experimental data (dashed lines) uses the aggregation model based on eqs 3 and 4.

Aggregation processes that would produce the observed concentration dependence have been proposed for a variety of acid−base systems in acetonitrile.[4c,17a,18,19] Ion pairing (or heteroconjugation, see eq 4) is the simplest case. This equilibrium by itself will influence the slope of the plot of E_{BH^+} vs log([base]/[acid]) but will not produce the sigmoidal dependence shown in Figure 6. We therefore built a combined regression model accounting for both eqs 3 and 4 (shown by the dashed line in Figure 7). Other possible aggregation reactions affording this dependence are considered in the Supporting Information. These models permit interpolation of Q, allowing OCP values to be estimated using eq 2. An example is provided below. Our choice of $^{n}Bu_4N^+PF_6^-$ as electrolyte for these studies was motivated by its prevalence; in light of the ion pairing interactions hypothesized for $[(DMF)H]^+OTf^-$, future study of electrolyte effects on OCP values may prove useful.

$$BH^+ + A^- \underset{}{\overset{K_{BHA}}{\rightleftharpoons}} BHA \qquad (4)$$

Determination of E_{BH^+} in Conjunction with Catalysis Studies. The results above demonstrate that the OCP is the equilibrium potential E_{BH^+} for a system in which acids and reducing equivalents interconvert with bases and hydrogen. While the method is useful for examination of complex acid−base equilibria, our primary goal is to measure equilibrium potentials E_{BH^+} for H_2 production and oxidation under conditions employed for catalysis, for the precise determination of overpotentials. Two examples are presented below, hydrogen evolution with $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$ and hydrogen oxidation with $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$.

Figure 8A shows voltammograms obtained with $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$, before and after adding 1:1 $[(DMF)H]^+OTf^-$:DMF, and after adding water, both in quantities affording maximum turnover frequencies. Under H_2 but in the absence of added acid or water, two reversible one-electron reductions are observed, assigned to the Ni(II/I) and Ni(I/0) couples (black trace). On addition of 1:1 $[(DMF)H]^+OTf^-$:DMF (0.40 M), a catalytic wave for the reduction of protons to H_2 is observed near the Ni(II/I) couple (red trace). Adding water (0.11 M) significantly increases the catalytic current (blue trace). These features have been discussed in detail elsewhere.[3b] Of primary importance for this work is the measurement of overpotentials at $E_{p/2}$ for this catalytic system.

Potentials for reversible H_2 oxidation/production were established by OCP measurements at Pt electrodes (Figure 8B)

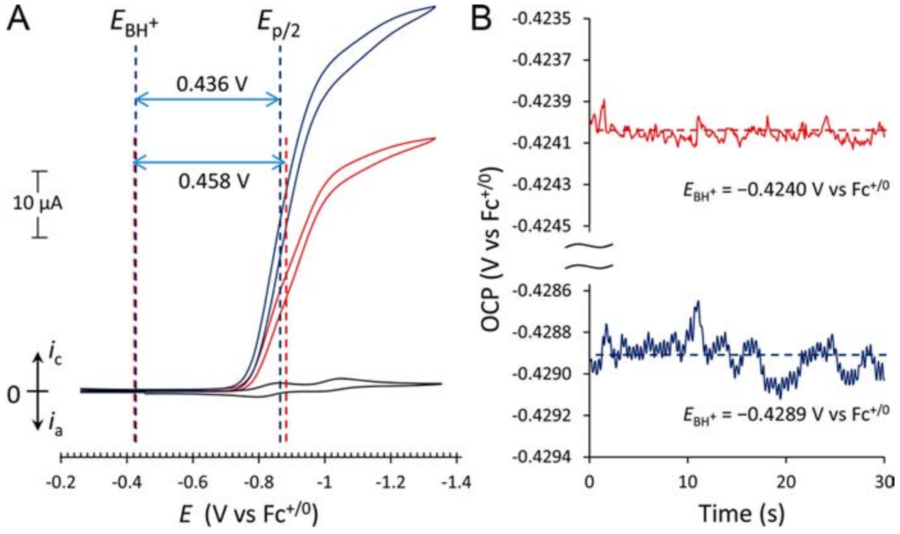


Figure 8. (A) Cyclic voltammograms of $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$ in acetonitrile ($^{n}Bu_4N^+PF_6^-$) under H_2 (1 atm, black trace), with 1:1 $[(DMF)H]^+OTf^-$:DMF (0.40 M, red trace) and with both $[(DMF)H]^+OTf^-$:DMF and water (0.40 and 0.11 M respectively, blue trace), collected with υ = 0.1 V s^{-1}. $E_{p/2}$ denotes the half-peak potentials of the catalytic waves. E_{BH^+} denotes the equilibrium potentials for reaction 1. (B) OCP of a platinum electrode vs $Fc^{+/0}$ as a function of time, used to determine E_{BH^+} for the solution compositions denoted by the colors shown in part A.

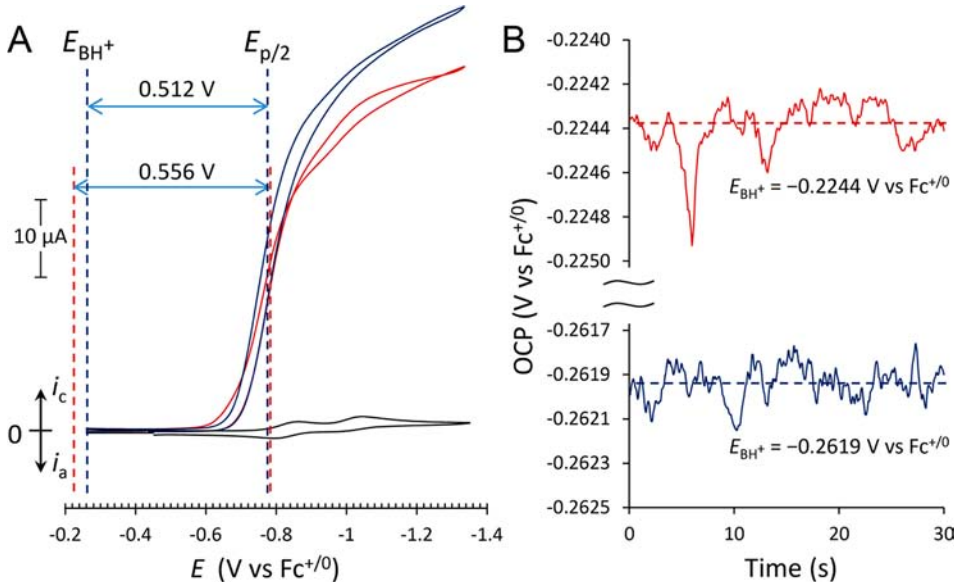


Figure 9. (A) Cyclic voltammograms of $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$ in acetonitrile ($^nBu_4N^+PF_6^-$) under H_2 (1 atm, black trace), with $[(DMF)H]^+OTf^-$ (0.4 M, red trace) and with both $[(DMF)H]^+OTf^-$ and water (0.4 and 0.11 M respectively, blue trace), collected with $\upsilon = 0.1$ V s^{-1}. $E_{p/2}$ denotes the half-peak potentials of the catalytic waves. E_{BH^+} denotes the equilibrium potentials for reaction 1. (B) OCP of a platinum electrode vs $Fc^{+/0}$ as a function of time, used to determine E_{BH^+} for the solution compositions denoted by the colors shown in part A.

of solutions having the same composition as those used for catalysis (Figure 8A). The OCP values in the presence and absence of water differ by only 5 mV. These potentials, labeled E_{BH^+} in Figure 8A, are subtracted from the half-peak potentials of the catalytic waves to afford overpotentials at $E_{p/2}$ for $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$ for these conditions. Turnover frequencies measured in our current studies reproduce prior results obtained in the absence of H_2 (250 s^{-1} without added water and 560 s^{-1} with added water),[3b] indicating that hydrogen does not influence the turnover frequency, consistent with the standard-state free energy change of 9 kcal mol^{-1} for hydrogen addition to $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2]^{2+}$ determined in previous studies.[22]

Most studies of electrocatalytic proton reduction to evolve H_2 are carried out by adding acids, but in the absence of added conjugate base. We therefore characterized catalysis with $[(DMF)H]^+OTf^-$, but without added DMF, the conjugate base of the buffered pair (Figure 9), using the same catalyst, acid, and water concentrations as shown above.

As expected, the OCP value is much more sensitive to added water in this case, changing by 38 mV compared to 5 mV for the buffered solution of acid. The OCP is stable both with and without water, possibly due to basic impurities. Minor impurities, while complicating the characterization of acid−base equilibria or the estimation of $E^\circ_{H^+}$, do not influence overpotential determinations, provided the solvent and other constituents employed are identical for both catalysis and OCP measurements. Since no base is initially present, the ratio of activities of acid and base at the electrode will change with time in an unstirred solution and may become quite different from that of the bulk solution. Artero's method for overpotential determination addresses this situation, as is discussed below.[3a] The cyclic voltammogram obtained without added water shows a curve crossing that was not evident after water was added; this behavior was reproducible over several repeated scans and at different scan rates and catalyst concentrations and may reflect an induction period associated with the initial absence of base in the solution; this phenomenon is beyond the scope of the present work.

Overpotentials at $E_{p/2}$ for both sets of experiments, determined using OCP measurements, eq 2, the method reported by Evans and co-workers,[5g] and the method of Artero and co-workers,[3a] are compared in Table 2. With the 1:1 acid:base mixture, overpotentials determined using OCP measurements are 35−40 mV smaller than the estimates afforded using eq 2 with the assumption that $Q = 1$, due to the concentration effects discussed above. Accounting for the aggregation reactions shown in eqs 3 and 4 affords an estimate of $Q = 5.2$ (see the Supporting Information), and the revised estimates using eq 2 are within 4 mV of the OCP-based values. Overpotentials determined using OCP measurements are considerably larger when only $[(DMF)H]^+OTf^-$ is added to the solution than when the 1:1 acid:base mixture is added. The value of E_{BH^+} estimated according to ref 3a produces overpotentials at $E_{p/2}$ that are smaller than the OCP-determined value by 228 (without water) and 190 mV (with water).

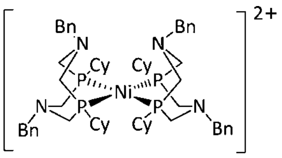
Electrocatalytic oxidation of hydrogen was examined with $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$ in acetonitrile ($^nBu_4N^+PF_6^-$) under hydrogen with 1:1 and 1:10 $Et_3NH^+BF_4^-$:Et_3N mixtures, and with subsequent addition of water (Figure 10). Reduction of $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$ in acetonitrile under N_2 (black trace) shows a reversible Ni(II/I) redox couple. Under H_2, oxidation (red trace) becomes irreversible and new waves are observed for the isomers formed upon addition of H_2 to $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$.[23] Subsequent introduction of Et_3N results in a catalytic wave corresponding to the electrocatalytic oxidation of H_2 (orange trace). The catalytic current is not appreciably affected by the presence of added $Et_3NH^+BF_4^-$ (0.1 equiv with respect to base, purple trace) and increases when the acid and base are equimolar (green trace). Water increases the catalytic current slightly (blue trace). The latter enhancements are attributed to isomer redistribution, as discussed elsewhere.[24] Table 3 presents a comparison of overpotentials using the different methods discussed herein.

The Nernst equation (eq 2) and the OCP method produce values of E_{BH^+} that agree within 12 mV, indicating that either the direct measurement or eq 2 with suitable inputs may be used to obtain reliable values of E_{BH^+}. The method reported in

Table 2. Overpotentials at $E_{p/2}$ (Bold) Evaluated by Several Methods, for Hydrogen Evolution Catalyzed by $[Ni(P^{Ph}_2N^{Ph}_2)_2](BF_4)_2$ in Acetonitrile (0.1 M $^nBu_4N^+PF_6^-$)

method		1:1 $[(DMF)H]^+OTf^-$:DMF (0.40 M each) no added water	1:1 $[(DMF)H]^+OTf^-$:DMF (0.40 M each) $[H_2O]$ = 0.11 M	$[(DMF)H]^+OTf^-$ (0.40 M) no added water	$[(DMF)H]^+OTf^-$ (0.40 M) $[H_2O]$ = 0.11 M
	$E_{p/2}$ (V vs $Fc^{+/0}$)	−0.882	−0.865	−0.784	−0.784
open circuit potential (OCP; this work)	E_{BH^+} (V vs $Fc^{+/0}$)	−0.424	−0.429	−0.224	−0.262
$E^\circ_{H^+}$ not required	**OP (V)**	**0.458**	**0.436**	**0.560**	**0.522**
eq 2[a]	E_{BH^+} (V vs $Fc^{+/0}$)	−0.389	−0.389	*b*	*b*
$E^\circ_{H^+}$ = −0.028 V vs $Fc^{+/0}$	**OP (V)**	**0.493**	**0.476**		
eq 2, accounting for aggregation[c]	E_{BH^+} (V vs $Fc^{+/0}$)	−0.428	−0.428		
$E^\circ_{H^+}$ = −0.028 V vs $Fc^{+/0}$	**OP (V)**	**0.454**	**0.437**		
ref 5g[d]	E_{BH^+} (V vs $Fc^{+/0}$)	−0.506	−0.506	−0.506	−0.506
$E^\circ_{H^+}$ = −0.145 V vs $Fc^{+/0}$	**OP (V)**	**0.376**	**0.359**	**0.278**	**0.278**
ref 3a	E_{BH^+} (V vs $Fc^{+/0}$)	*e*	*e*	−0.452	−0.452
$E^\circ_{H^+}$ = −0.070 V vs $Fc^{+/0}$	**OP (V)**			**0.332**	**0.332**

[a] Assuming that activities and concentrations are equal. [b] Equation 2 is not defined for these conditions. [c] See eqs 3 and 4, the associated text above, and the Supporting Information for estimation of aggregation equilibrium constants. [d] This value of $E^\circ_{H^+}$ was amended in ref 5g from a value presented in ref 5f. [e] This method estimates E_{BH^+} at the electrode for cases when catalysis is first order in [acid], and with no deliberately added base or hydrogen.



$[Ni(P^{Cy}_2N^{Bn}_2)_2]^{2+}$

ref 5g affords better agreement with the 1:10 acid:base mixture than with the 1:1 mixtures, due to cancellation of errors associated with the value of $E^\circ_{H^+}$ employed and with the assumption that the bulk solution composition does not influence the ratio of acid to base at the electrode surface at $E_{p/2}$. Adding water does not appreciably affect the OCP values for these buffered solutions.

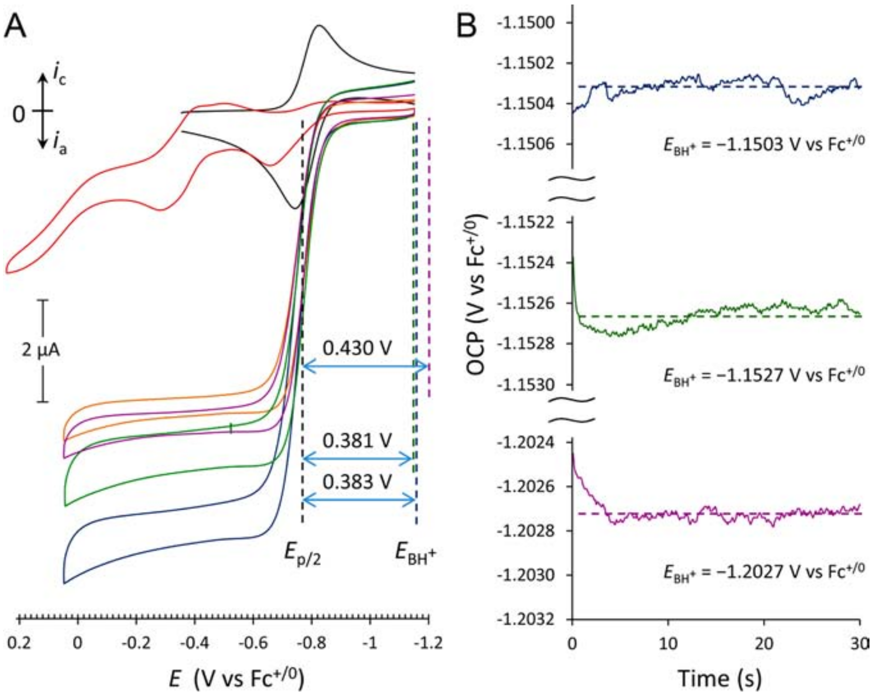


Figure 10. (A) Cyclic voltammograms of $[Ni(P^{Cy}_2N^{Bn}_2)_2](BF_4)_2$ in acetonitrile ($^nBu_4N^+PF_6^-$) (black trace), under H_2 (1.0 atm, red trace), with Et_3N (33 mM, orange trace), with Et_3N and $Et_3NH^+BF_4^-$ (31 and 3.1 mM respectively, purple trace; 20 mM for both, green trace) and with with Et_3N and $Et_3NH^+BF_4^-$ (20 mM) and water (0.16 M, blue trace), collected with υ = 0.1 V s^{-1}. $E_{p/2}$ denotes the half-peak potentials of the catalytic waves. E_{BH^+} denotes the equilibrium potentials for reaction 1. (B) OCP of a platinum electrode vs $Fc^{+/0}$ as a function of time, used to determine E_{BH^+} for the solution compositions denoted by the colors shown in part A.

Table 3. Overpotentials at $E_{p/2}$ (Bold) by Several Methods, for Hydrogen Oxidation Catalyzed by $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$ in Acetonitrile (0.1 M $^nBu_4N^+PF_6^-$)

		Et_3N (31 mM) + $Et_3NH^+BF_4^-$ (3.1 mM)	Et_3N (20 mM) + $Et_3NH^+BF_4^-$ (20 mM)	
method		no added water	no added water	$[H_2O]$ = 0.11 M
	$E_{p/2}$ (V vs $Fc^{+/0}$)	−0.773	−0.772	−0.767
open circuit potential (OCP; this work)	E_{BH^+} (V vs $Fc^{+/0}$)	−1.203	−1.153	−1.150
$E^\circ_{H^+}$ not required	**OP (V)**	**0.430**	**0.381**	**0.383**
eq 2[a]	E_{BH^+} (V vs $Fc^{+/0}$)	−1.200	−1.141	−1.141
$E^\circ_{H^+}$ = −0.028 V vs $Fc^{+/0}$	**OP (V)**	**0.427**	**0.369**	**0.374**
ref 5g[b]	E_{BH^+} (V vs $Fc^{+/0}$)	−1.258	−1.258	−1.258
$E^\circ_{H^+}$ = −0.145 V vs $Fc^{+/0}$	**OP (V)**	**0.485**	**0.486**	**0.491**

[a] Assuming that activities and concentrations are equal. [b] This value of $E^\circ_{H^+}$, reported in ref 5g, amends a value originally appearing in ref 5f.

OCP Values of Solutions of $[(DMF)H]^+OTf^-$ Under Hydrogen with No Added Base and of Et_3N Under Hydrogen with No Added Acid. As mentioned above, hydrogen production electrocatalysis is typically examined in the absence of added base or hydrogen. To permit estimation of overpotentials for cases where $[(DMF)H]^+OTf^-$ was used as the acid, we examined the OCP values of unbuffered solutions of this acid under hydrogen, using acetonitrile purified as described above. The acid concentration was varied in twenty increments from 0 to 0.40 M. A plot of OCP vs log([[(DMF)H]$^+$]) afforded a linear fit (Supporting Information, Figure S5A) with R^2 = 0.9983 (eq 5, with [[(DMF)H]$^+$] in moles per liter). Hydrogen is required for the open circuit measurement, and

$$\text{OCP (V vs Fc}^{+/0}) = 0.0720 \log([[(\text{DMF})\text{H}]^+]) - 0.192 \qquad (5)$$

so the use of eq 5 to estimate equilibrium potentials for experiments carried out without base *or* hydrogen implies the assumption that hydrogen itself does not influence $E_{p/2}$. This assumption, which holds for $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$, should be considered for each catalyst system examined.

This series of measurements and the catalysis experiments shown in Figure 9 were executed at different times with different batches of solvent, substrate, and electrolyte. The OCP value measured with [acid] = 0.40 M was −0.2195 V vs $Fc^{+/0}$ in the absence of catalyst, 5 mV positive of the value obtained during the catalysis study. With acid but no Brønsted base added deliberately to the solution, the value of Q in eq 2 will be close to zero at equilibrium, and since $d \ln(Q) = dQ/Q$, small variations in Q will cause large changes in $\ln(Q)$ and the OCP will be very sensitive to variations in α_B due to adventitious base. This noise in the value of $\ln(Q)$ at very large (or very small) values of Q underscores that the OCP measurement, like any equilibrium determination, is more reliable when the participant species are at similar activities. In addition, the effect of an electrocatalytic process on the solution composition at the electrode will be larger when Q is very large or very small. This is examined further in the Discussion section.

We also measured OCP values for solutions of Et_3N in acetonitrile ($^nBu_4N^+PF_6^-$) under H_2 with no deliberately added proton source, again using the acetonitrile distilled first from H_2SO_4 and then from CaH_2, in order to estimate overpotentials for previously reported hydrogen oxidation catalysis studies. $[Et_3N]$ was varied in ten increments from 0 to 0.071 M (the catalysis experiments exemplified by Figure 10 generally employ base concentrations in this range), and then in ten additional increments from 0.071 to 0.773 M. A plot of OCP values vs log($[Et_3N]$) afforded a linear fit (Supporting Information, Figure S5B) with R^2 = 0.9989 (eq 6 with $[Et_3N]$ in moles per liter).

$$\text{OCP (V vs Fc}^{+/0}) = -0.0548 \log([\text{Et}_3\text{N}]) - 1.407 \qquad (6)$$

The stability of these measurements and the linearity of OCP vs log($[Et_3N]$) is assumed to derive from the presence of trace quantities of some proton source in solution. The measured OCP with $[Et_3N]$ = 7.2 mM (the lowest concentration measured) was −1.291 V vs $Fc^{+/0}$. Rearranging eq 2 and inputting $E^\circ_{H^+}$ = −0.028 V vs $Fc^{+/0}$ and the pK_a value of 18.82 for Et_3NH^+, one obtains an estimate of $[Et_3NH^+]$ = 0.02 mM.

Equation 6 may be used to estimate OCP values for previously reported experiments. For example, hydrogen oxidation catalyzed by $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$ was previously reported in the presence of 0−8.6 mM Et_3N, having $E_{p/2}$ = −0.73 V vs $Fc^{+/0}$ with $[Et_3N]$ = 8.6 mM.[10c] According to eq 6, the OCP for these conditions would have been approximately −1.29 V vs $Fc^{+/0}$ affording an overpotential at $E_{p/2}$ of 0.56 V.

DISCUSSION

For an electrocatalyst mediating a half-reaction in an electrochemical cell, energy efficiency is evaluated by the relationship between current and overpotential. In homogeneous electrocatalytic systems, the response of the current to a sweep in potential often approaches a sigmoidal dependence, as shown in Figure 1. Turnover frequencies are calculated straightforwardly from catalytic currents by invoking a steady-state approximation, so catalytic studies often employ conditions in which the current (and hence the rate) is pseudo-zero-order in substrate (Figures 8−10).[1,2b,3b,10] The value of E_{BH^+} can and should be obtained under the same conditions as those used to determine turnover frequencies, ideally from the same solutions. However, studies of electrocatalytic reactions are often conducted with the catalytic substrates, but not the products, added deliberately to the solution: for example, hydrogen production is often studied by adding only acid (but no base) to the catalyst solution. While this may afford steady-state kinetics (absent product inhibition, induction, catalyst decomposition, or other effects), conditions at the electrode may differ from those of the bulk solution and may change with time, even in cases where a constant current is observed. Precise determination of E_{BH^+} (and hence overpotentials) at the electrode using either the Nernst equation or the OCP method requires conditions wherein the activities of acid, base, and hydrogen *all* adhere to a steady-state approximation.

As noted above, measuring overpotentials at the half-peak potential $E_{p/2}$ of the catalytic wave is appropriate for characterizing systems whose responses approach kinetic control, and this standard has been adopted by many researchers.[3a,5g] A commonly used method, formulated by Evans and co-workers,[5g] compares $E_{p/2}$ to the standard state potential $E^{\circ}_{BH^+}$ for reaction 1, computed according to Scheme 1.[5d] This assumes that at $E_{p/2}$ in the region near the electrode where heterogeneous redox occurs, $\alpha_{BH^+} = \alpha_B$ and $\alpha_{H2} = 1$ (thus $Q = 1$; see eq 2), regardless of the initial conditions. Increasing the analytical concentration of BH^+ will certainly increase α_{BH^+} at the electrode, but may or may not influence i_p or $E_{p/2}$. Moreover, if only acid is added, α_{BH^+} and α_B will become equal at some point during the potential sweep only if catalysis is very rapid compared to substrate and product diffusion, as with rapid catalysis under high catalyst loading (for example, "total catalysis").[1] The potential at which this occurs does not necessarily coincide with $E_{p/2}$. Artero and co-workers have also addressed the issue of estimating Q at the electrode surface under substrate diffusion-limited (i.e., nonsteady-state) conditions.[3a] The method as described is limited to cases where the reaction is first-order in acid and relies on $E^{\circ}_{H^+}$, pK_a, and the diffusion coefficients of the acid, base, and hydrogen and, in cases where aggregation is possible, the equilibrium constants for the aggregation reactions. Moreover, estimating the solution composition at the electrode under nonsteady-state conditions and taking this as the relevant composition for overpotential determination neglects the work required to establish the substrate and product concentration gradients. The complexities and limitations associated with these methods underscore the advantages of using a steady-state approximation wherein Q at the electrode is essentially equal to Q in the bulk solution throughout the course of the voltammetry experiment.

In this paper, we establish that equilibrium potentials for reaction 1, the interconversion of proton donors and electrons with proton acceptors and hydrogen, may be measured using the OCP method for acetonitrile electrolyte solutions. This constitutes a general method for obtaining equilibrium potentials as a basis for overpotential determination in catalytic systems. The data presented here also yield the potential of the SHE in acetonitrile vs the $Fc^{+/0}$ couple. Our desire for accuracy in this value motivated consideration of factors such as solvent impurities and solute nonideality, effects that "cancel out" in an overpotential determination. Here, precision may be obtained by performing open circuit measurements and catalysis measurements using solutions of the same composition, prepared with material from the same sources.

Standard Hydrogen Electrode in Acetonitrile. The potential $E^{\circ}_{H^+}$ for the interconversion of a solvated proton at unit activity with hydrogen, also at unit activity, is essential for determining acidities, hydride donor abilities, and bond dissociation free energies using thermochemical cycles that include redox reactions.[5d] The weak basicity of acetonitrile precludes direct observation of this reaction; however, the established pK_a scale permits the estimation of $E^{\circ}_{H^+}$ using Scheme 1 and examining the OCP values of acid–base mixtures in the limit of infinite dilution. The value obtained by this method is in good agreement with the value reported in 1965 by Kolhoff and Thomas,[5c] also based on OCP measurements but using sulfuric acid–bisulfate as the analyte, and with thermochemical cycles reported by Wayner and Parker and DuBois and co-workers (Table 4).

Table 4. Reported and Present Values of $E^{\circ}_{H^+}$ for Acetonitrile, in Order of Precedence

$E^{\circ}_{H^+}$ (V vs $Fc^{+/0}$)	method	source
−0.034	OCP measurements using sulfuric acid:bisulfate	ref 5c
−0.26	cyclic voltammetry of perchloric acid	ref 5f
−0.05	a thermochemical cycle constructed using the potential of the hydrogen electrode in water	ref 5d
−0.07	a thermochemical cycle using hydride donor abilities, pK_a values, and 2-electron redox potentials for a series of Pt and Ni hydrides	refs 5a and 5b
−0.14	correction to the value presented in ref 5f to account for incomplete dissociation of perchloric acid	ref 5g
−0.07	correction to the value presented in ref 5f to account both for incomplete dissociation of perchloric acid and for concentration effects	ref 3a
−0.028[a]	OCP measurements using a series of acids over a range of solution compositions	this work

[a] Standard deviation is 4 mV across measurements from four different acid–base systems.

Direct Measurement vs Calculation using the Nernst Equation. OCP measurements require careful preparation but no unusual equipment; due to the oxygen sensitivity of the platinum surface, they are best carried out within a glovebox having feedthroughs for hydrogen gas and potentiostat leads. While the OCP measurement is more precise for overpotential determination, the Nernst equation with suitable inputs will provide more facile access to E_{BH^+}. Table 3 presents overpotentials at $E_{p/2}$ for hydrogen oxidation catalyzed by $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$ with acetonitrile as the reaction medium. Values of E_{BH^+} were obtained both by direct OCP measurement and using eq 2 with $E^{\circ}_{H^+} = -0.028$ V vs $Fc^{+/0}$ and the assumption that the analytical concentrations of Et_3N and $Et_3NH^+BF_4^-$ are equal to their activities. The agreement between these methods is as expected and should be accurate inasmuch as the activity–concentration assumption holds; this will be true in general for acids that do not undergo homoconjugation or other aggregation reactions, such as Et_3N, aniline, and *para*-toluidine.[16a,18]

Accounting for aggregation reactions becomes necessary when their influence on equilibrium potentials is large compared to the desired precision of the measurement. This is shown in Table 2, listing overpotentials at $E_{p/2}$ for hydrogen production mediated by $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2]^{2+}$ with buffered and unbuffered $[(DMF)H]^+OTf^-$ as substrate: Values of E_{BH^+} obtained by OCP measurements differ by 35−40 mV from values obtained using eq 2 with the activity–concentration assumption. It is also illustrated in Figure 7, showing values of E_{BH^+} that span 50 mV for 1:1 mixtures of $[(DMF)H]^+OTf^-$ and DMF at various concentrations. Modeling of aggregation equilibria (eqs 3 and 4 above) allows interpolation of values of Q for the conditions used for catalysis; calculations using eq 2 with these estimates of Q afford values of E_{BH^+} that agree within 5−10 mV of the direct OCP measurements. Aggregation equilibrium constants are accessible using a variety of analytical methods.[17−21]

Overpotential at $E_{p/2}$ as a Function of the Reaction Medium. The OCP method is valuable for determining equilibrium potentials, and thus comparing overpotentials in different electrolyte solutions, including those for which there is no pK_a scale at present, e.g. fluorobenzene[25] and in novel media such as ionic liquids.[7] For example, we have previously used the OCP method to establish overpotential scales in mixtures of water with the ionic liquid dibutylformamidium bis(trifluoromethanesulfonyl)amide[8] and may now make a direct comparison between the overpotentials at $E_{p/2}$ obtained in these media with those obtained in acetonitrile. The OCP of the ionic liquid−water mixture having a mole fraction of 0.72 in water was determined to be −0.219 V vs $Fc^{+/0}$. Proton reduction catalyzed by $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$ has an overpotential at $E_{p/2}$ of 0.420 V in this medium. For comparison, an OCP value of −0.224 V vs $Fc^{+/0}$ was measured for a 0.4 M solution of $[(DMF)H]^+OTf^-$ in acetonitrile without added water, affording an overpotential at $E_{p/2}$ of 0.560 V for the same catalyst (Table 2). With added water (0.1 M), the OCP value was −0.262 V vs $Fc^{+/0}$ and the overpotential at $E_{p/2}$ was 0.522 V. This comparison underscores the significance of the reaction medium not only in determining catalytic rates (in this case faster in the ionic liquid by a factor of 10), but on overpotential as well (lower at $E_{p/2}$ by 100 mV). This comparison also illustrates the generality of basing overpotential scales on values of E_{BH^+} measured by the OCP method for the bulk solution as employed for catalysis. Use of the OCP method with new media does require establishing that reaction 1 alone governs the potential. Measurement across a range of solution compositions and reconciling the results with the Nernst equation accomplishes this goal. A single-point measurement is not sufficient for this purpose. However, provided the range of compositions examined encompasses those used for catalysis, the data acquired, along with the model constructed, allows estimation of E_{BH^+} for any number of catalysis studies without requiring that each new study be accompanied by a series of OCP measurements.

A final point to be made regarding overpotential measurements is that these values contain contributions that are intrinsic to the catalyst (reaction kinetics and the redox properties of catalytic intermidiates) and those that are not (factors influencing E_{BH^+}). In the examples given above, the catalytic studies were often conducted under conditions that would provide useful mechanistic insights into the different catalysts under study. For example, the use of triethylamine (pK_a = 18.8 for Et_3NH^+ in acetonitrile)[4c] in the studies of H_2 oxidation using $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$ as the catalyst is convenient in that deprotonation of the catalytic intermediates is complete, because the pK_a value of Et_3NH^+ is much larger than the pK_a values of the protonated catalytic intermediates (approximately 13.4 for this particular catalyst).[22] While the use of a strong base simplifies mechanistic studies and enriches our understanding of these catalysts, it results in larger extrinsic contributions to the overpotential. In principle, weaker bases than triethylamine could be used with lower pK_a values (approaching 13.4 for $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$) and lower overpotentials could be obtained. A precise, flexible, and universal method for determination of overpotential should allow practitioners to develop and share insights leading to the optimization of this important parameter and ultimately to a deeper understanding of the relationship between rate and overpotential for molecular electrocatalysts.

CONCLUSIONS

Open circuit potential (OCP) measurements are a powerful method for the direct determination of equilibrium potentials for the interconversion of acids and electrons with bases and hydrogen. The measurements of acetonitrile solutions presented here afford a revised value for the standard hydrogen electrode (SHE) in this medium. The method works for a broad range of different acid−base systems, and the results agree with values of E_{BH^+} computed using the Nernst equation for systems wherein the equilibrium ratio of acid and base activities may be estimated. In other cases, information regarding complex acid−base equilibria are obtained.

Establishing adherence to the Nernst equation is essential in validating the OCP measurements. Use of OCP measurements with new acid−base systems and new media therefore requires examination of a range of different solution compositions. Validation *does not* require a pK_a scale or an estimate of the SHE for the medium in question, only that measured potentials respond to changes in solution composition according to the Nernst equation.

The use of measured or, when appropriate, calculated values of E_{BH^+} as a basis for overpotential determination removes assumptions regarding the activities of participant species at the electrode surface and constitutes a rigorous basis for the determination of overpotentials for electrocatalytic hydrogen oxidation and production systems operating with all participants at steady state. This allows comparison of overpotentials across widely disparate reaction conditions, opening the way for systematic exploration of the influence of solvent, substrate, hydrogen pressure, temperature, and coreactant species on overpotential.

EXPERIMENTAL SECTION

Materials and Methods. Schlenk techniques or an inert-atmosphere glovebox were used for all manipulations. Acetonitrile (Alfa-Aesar, anhydrous, amine-free), dichloromethane (Fisher, not stabilized), and diethyl ether (VWR, not stabilized) were purified by sparging with nitrogen and passage through neutral alumina using a solvent purification system (PureSolv, Innovative Technologies, Inc.). Acetonitrile was further purified by short-path distillation (1 atm) from sulfuric acid (99.999% metals basis, Aldrich) and then by fractional distillation from calcium hydride (Aldrich) using a 50 cm Vigreux column and a variable reflux ratio distillation head (T_h = 80.4−80.5 °C). The first 10% of distillate was discarded, and the distillation was terminated at ~90% completion.[16b] This acetonitrile was used for the dilution studies described below. Tetrabutylammonium hexafluorophosphate ($^nBu_4N^+PF_6^-$) was prepared from $^nBu_4N^+I^-$ and $NH_4^+PF_6^-$ (Aldrich) and purified by crystallization from saturated acetone solution.[26] Ferrocene (Fc, Aldrich) was purified by sublimation. (Permethylferrocene Fc*, Aldrich) and permethylcobaltocenium hexafluorophosphate (Strem) were used as received. Hydrogen (Oxarc UHP; 99.999%) was purified by passage through a water/oxygen/hydrocarbon trap (Restek 22464) and an indicating water/oxygen trap (Restek 22474) and fed through the glovebox wall. Water was dispensed from a Millipore Milli-Q purifier (18 MΩ cm^{-1}) and sparged with nitrogen. Dimethylformamide (DMF; Burdick and Jackson) was used as received. Trifluoromethanesulfonic acid (HOTf; Aldrich, 99%) was used as received and handled under nitrogen. $[(DMF)H]^+OTf^-$ was preprared by literature methods.[27] Triethylamine (Et_3N, Aldrich) was fractionally distilled (T_h = 88.7−88.8 °C). Tetrafluoroboric acid etherate ($HBF_4{\cdot}Et_2O$, Aldrich) was used as received and stored at −35 °C in the glovebox. 4-Bromoaniline ($4\text{-}BrC_6H_4NH_2$, Aldrich) and 4-cyanoaniline ($4\text{-}NCC_6H_4NH_2$, Aldrich) were sublimed. 2,6-Dichloroaniline ($2,6\text{-}Cl_2C_6H_3NH_2$, Aldrich) and 4-anisidine ($4\text{-}MeOC_6H_4NH_2$, Aldrich) were sublimed then recrystallized from diethyl ether until colorless. $Et_3NH^+BF_4^-$, $4\text{-}NCC_6H_4NH_3^+BF_4^-$, $2,6\text{-}Cl_2C_6H_3NH_3^+BF_4^-$, $4\text{-}BrC_6H_4NH_3^+BF_4^-$, and $4\text{-}MeOC_6H_4NH_3^+BF_4^-$ precipitated on slow addition of $HBF_4{\cdot}Et_2O$ to an Et_2O solution of ~5% excess base. $4\text{-}NCC_6H_4NH_3^+BF_4^-$ and $4\text{-}MeOC_6H_4NH_3^+BF_4^-$ were further purified by recrystallization from acetonitrile/ether. $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$ and $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$ were prepared by literature procedures.[10c]

Analytical Methods. Stock solutions were prepared as needed using volumetric glassware and gastight syringes in the glovebox and were used immediately. Solid and liquid solutes were quantitated by mass. Electrochemical measurements were conducted using a CH Instruments 620D potentiostat using the four-electrode cell shown in Figure 2. The working electrode used for cyclic voltammetry was a

1 mm glassy carbon disk encased in polyether−ether−ketone (PEEK; ALS), cleaned as needed inside the glovebox using a polishing pad (Buehler MicroCloth) loaded with diamond paste (Buehler MetaDi II 0.25 μm) and lubricated with ethylene glycol (Aldrich), followed by rinsing with acetonitrile. A fresh portion of the polishing pad was used for each polishing operation. The counterelectrode used for cyclic voltammograms was a 3 mm diameter glassy carbon rod (Alfa Aesar). The pseudoreference electrode used for both cyclic voltammograms and open circuit potential (OCP) measurements was a silver wire (Alfa Aesar; 1 mm dia., 99.9%) cleaned with abrasive paper, anodized for 5 min in aqueous HCl (Aldrich), washed with water and acetone, dried, and suspended in a glass tube containing neutral acetonitrile ($^n\mathrm{Bu_4N^+PF_6^-}$, at the same ionic strength as the analyte solution) and fitted with a porous Vycor disc using fluorinated ethylene propylene heat-shrink tubing. Storage of the reference electrodes in a ball-and-socket storage tube containing electrolyte solution and sealed with a Kalrez O-ring preserved their function essentially indefinitely. The potential of the reference electrode (E_{ref}) vs $\mathrm{Fc^{+/0}}$ generally changed by less than 25 mV over a given set of measurements.

The platinum wire electrodes used for OCP (Alfa Aesar; 99.95%, 1 mm diam, ~50 mm length) were prepared by rinsing with acetone, drying in air, immersing in freshly prepared aqua regia for 30 min, then rinsing with flowing deionized water (18 MΩ cm^{-1}) for 5 min. Each wire was then clamped into a stainless steel hemostat and heated to a uniform yellow-orange glow in a hydrogen-air flame (Smith Little Torch, no. 6 tip, flame length ~10 cm). Once the entire wire was at the maximum temperature attainable (judged by color), the flame was extinguished and the wire was allowed to cool in the hydrogen stream until it no longer glowed. At this point, the wire was placed in a screw-cap storage tube maintained under a positive flow of nitrogen. After each wire was treated, the tube was closed and taken into the glovebox. Each wire was useable for at least several measurements, sometimes affording consistent data for up to a day. Unused electrodes remained active for several days if stored in the glovebox. Excessive and increasing signal noise, leading ultimately to a substantial instability of the OCP, were generally taken to indicate deterioration of the electrode response, and the electrode was replaced. Substitution of one electrode with another afforded the same OCP value within 3 mV. The same set of four platinum wire electrodes was reconditioned as described above and reused numerous times with no effect on the OCP measurements. Contamination with oxygen caused rapid deterioration of the OCP response: measurements conducted after the O_2 capacity of the O_2/H_2O traps had been exhausted revealed a rapid deterioration of the signal-to-noise ratio. This was interpreted as passivation of the platinum surface by oxygen.

Measurement of OCP vs $\mathrm{Fc^{+/0}}$. A new, oven-dried 1 dram shell vial containing a stirbar and fitted with a polyethylene cap with openings for the electrodes and gas inlet tube (Figure 2) was charged with an analyte solution of the desired composition. One crystal of ferrocene (<0.5 mg) was added to the solution. The hydrogen gas stream was presaturated by bubbling through vigorously stirred acetonitrile and let into the cell via PEEK tubing (0.063 in o.d. × 0.030 in i.d.). The cell contents were sparged with hydrogen (5−10 bubbles per second) for several minutes with stirring. The stirring was briefly paused, and the hydrogen source tube was withdrawn to the headspace. A cyclic voltammogram spanning the $\mathrm{Fc^{+/0}}$ couple was recorded at the glassy carbon working electrode, using the reference electrode and the glassy carbon counter electrode. Stirring and sparging were reestablished, and a 30-s trace of the OCP between the reference and platinum wire electrodes was collected. This measurement was repeated until the OCP value from t = 5−30 s varied by less than 0.5 mV from the mean and showed no systematic drift in potential; 1−3 traces were typical for each OCP measurement. The equilibration time ranged from a few seconds to several minutes. Temperatures within the glovebox were generally between 24 and 27 °C. The elevation of Richland, WA is 117 m (384 ft); pressure above the solutions was assumed to be 1.0 atm for all experiments.

Deoxygenated water was added deliberately in some experiments (up to 1 M) and had no effect on the stability of the OCP. Use of the platinum wire as a working electrode for voltammetric determination of the $\mathrm{Fc^{+/0}}$ redox potential resulted in immediate degradation of the OCP response. Fouling of platinum surfaces under hydrogen in acetonitrile at potentials near that of the $\mathrm{Fc^{+/0}}$ couple is well-documented[13] and appears to involve formation of surface-bound $\mathrm{CN^-}$ groups. Reconditioning restored the OCP response.

OCP vs $\mathrm{Fc^{+/0}}$ as a Function of [Acid]:[Base]. These measurements were carried out for $\mathrm{[(DMF)H]^+OTf^-}$, $\mathrm{Et_3NH^+BF_4^-}$, 4-$\mathrm{BrC_6H_4NH_3^+BF_4^-}$, and 4-$\mathrm{NCC_6H_4NH_3^+BF_4^-}$. The general procedure is illustrated using the following example: A 0.50 M stock solution of $\mathrm{[(DMF)H]^+OTf^-}$ in acetonitrile was prepared by dissolving $\mathrm{[(DMF)H]^+OTf^-}$ (558.4 mg, 2.502 mmol) in acetonitrile and diluting to 5.0 mL. A stock solution of DMF (0.50 M) and $^n\mathrm{Bu_4N^+PF_6^-}$ (0.50 M) was prepared by diluting DMF (182.3 mg, 2.494 mmol) to 5.0 mL using acetonitrile (0.50 M $^n\mathrm{Bu_4N^+PF_6^-}$). A 1.0 mL portion of the acid solution and 0.10 mL of base solution were added to the cell. The above measurement sequence was executed. A 0.10 mL aliquot of base solution was then added to the cell, sparging was maintained for 1 min, and the measurement sequence was repeated. The solution composition was incremented in this way until the ratio of acid to base was 1:1. The entire measurement sequence was then repeated using the same stock solutions, beginning with 1.0 mL of base solution and 0.10 mL acid solution. A 1.0 mL portion each of the acid and base stock solutions were then diluted to a volume of 5.0 mL using acetonitrile (0.50 M $^n\mathrm{Bu_4N^+PF_6^-}$) to afford 0.1 M stock solutions, and the measurement sequences were repeated. Data for these experiments appears in Figures 4−6 and in Supporting Information Figures S1 and S2.

OCP vs $\mathrm{Fc^{+/0}}$ as a Function of Concentration with [Acid]:[Base] = 1:1. These measurements were executed using the redistilled acetonitrile (see the Materials and Methods subsection) with $\mathrm{[(DMF)H]^+OTf^-}$, $\mathrm{Et_3NH^+BF_4^-}$, 4-$\mathrm{MeOC_6H_4NH_3^+BF_4^-}$, and 2,6-$\mathrm{Cl_2C_6H_3NH_3^+BF_4^-}$. The following example shows the general procedure. An analyte solution was prepared as follows: $\mathrm{[(DMF)H]^+OTf^-}$ (111.3 mg, 0.499 mmol) and DMF (36.3 mg, 0.497 mmol) were combined and diluted to a volume of 1.0 mL, affording a solution of 0.50 M analytical concentration in both $\mathrm{[(DMF)H]^+OTf^-}$ and DMF. An electrolyte solution was then prepared, with $^n\mathrm{Bu_4N^+PF_6^-}$ (968.6 mg, 2.50 mmol) diluted to 5.0 mL. A crystal of ferrocene (<0.5 mg) was added to each. The above measurement sequence was executed with the 0.50 M analyte solution. A 0.20 mL aliquot of this solution was transferred to a new vial, and 0.80 mL of electrolyte solution was added, affording a new analyte solution of 0.10 M acid and base concentrations. The electrodes were rinsed, the cell cap fitted to the new cell, and the measurement sequence was repeated. This sequence was carried out over six sequential dilutions, affording analyte concentrations ranging from 0.50 M to 0.16 mM. Data are shown in Figure 7. For the purpose of estimating $E^{\circ}_{\mathrm{H^+}}$, the $\mathrm{Fc^{+/0}}$ and $\mathrm{Fc^{*+/0}}$ redox potentials are assumed to be invariant with solution composition.

Determination of $E_{\mathrm{BH^+}}$ in Conjunction with Catalysis Studies: Hydrogen Production Catalysis with $\mathrm{[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2}$. Stock solutions were prepared as follows: A 1.8 mg portion of $\mathrm{[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2\cdot CH_3CN}$ (1.5 mmol) was diluted to 2.0 mL in acetonitrile (0.1 M $^n\mathrm{Bu_4N^+PF_6^-}$) and one crystal of Fc (<0.5 mg) was added. An acid stock solution with $\mathrm{[(DMF)H]^+OTf^-}$ (447.1 mg, 2.00 mmol) diluted to 1.0 mL in acetonitrile was prepared, and a 1:1 acid:base stock solution was prepared by adding DMF (73.4 mg, 1.00 mmol) to 0.50 mL of the acid stock solution. Using a standard three-electrode cell (1 mm diameter glassy carbon working electrode, counter, and reference electrodes as described above), cyclic voltammograms were recorded following (1) addition of 0.80 mL of catalyst solution, (2) sparging for 2 min with acetonitrile-saturated hydrogen (this cyclic voltammogram and the first were nearly superimposable), (3) addition of 0.20 mL acid stock solution, affording a turnover frequency (TOF) of 420 s^{-1},[3b] and (4) addition of 2 μL deoxygenated water (TOF = 530 s^{-1}). The resultant solution was 0.40 M in acid and 0.1 M in water. Beginning with a 0.80 mL solution of ferrocene in acetonitrile (0.1 M $^n\mathrm{Bu_4N^+PF_6^-}$) *without* added catalyst, the above sequence of additions was repeated in a separate cell equipped for the four-electrode OCP experiment, with OCP and cyclic voltammogram measurements as described above performed after each addition. Data are shown in Figure 9. These experiments were then repeated using the 1:1 acid:base stock solution. Turnover frequencies were 250 s^{-1} with 1:1 acid:base (0.40 M) and 560 s^{-1} with added water (0.10 M). OCP values obtained by direct measurement of the solutions containing the catalyst were within 10 mV of those measured with the solutions without catalyst but were less stable.

Determination of E_{BH^+} in Conjunction with Catalysis Studies: Hydrogen Oxidation Catalysis with $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$. Stock solutions were prepared as follows: $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2](BF_4)_2$ (1.1 mg, 0.92 mmol) was diluted to 1.0 mL in acetonitrile (0.1 M $^nBu_4N^+PF_6^-$) and one crystal of permethylcobaltocenium hexafluorophosphate (<1 mg; for the $Co^{III/II}$ couple, $E_{1/2}$ = −1.904 V vs $Fc^{+/0}$) was added. An acid stock solution with $Et_3NH^+BF_4^-$ (47.6 mg, 0.252 mmol) and $^nBu_4N^+PF_6^-$ (97.0 mg, 0.250 mmol) diluted to 5.0 mL in acetonitrile was prepared. A base stock solution of Et_3N (25.3 mg, 0.250 mmol) diluted to 5.0 mL with acetonitrile (0.1 M $^nBu_4N^+PF_6^-$) was prepared. Cyclic voltammograms were recorded following (1) addition of 0.50 mL catalyst solution, (2) sparging 2 min with acetonitrile-saturated hydrogen, (3) addition of 1.0 mL base solution and 0.10 μL acid solution (the solution was then 31 mM in base and 3.1 mM in acid; TOF = 2.6 s^{-1}), (4) addition of 0.9 mL acid solution (TOF = 3.1 s^{-1}), and (5) addition of 0.5 μL deoxygenated water (TOF = 4.6 s^{-1}). The solution was then 20 mM in both base and acid and 0.16 M in water. Beginning with a 0.50 mL solution of permethylferrocene in acetonitrile (0.1 M $^nBu_4N^+PF_6^-$) *without* added catalyst, the above sequence of additions was repeated in a separate cell equipped for the four-electrode OCP experiment, with OCP and cyclic voltammogram measurements as described above performed after each addition. Data are shown in Figure 10.

OCP vs $Fc^{+/0}$ as a Function of $[[(DMF)H]^+OTf^-]$ with No Added Base. An electrolyte solution was prepared with $^nBu_4N^+PF_6^-$ (779.0 mg, 2.011 mmol) diluted to 10.0 mL using redistilled acetonitrile. 0.8 mL of electrolyte solution was transferred to a new vial and sparged with hydrogen and one crystal of ferrocene was added. An analyte solution was prepared by diluting $[(DMF)H]^+OTf^-$ (444.9 mg, 1.993 mmol) to 1.0 mL using redistilled acetonitrile. The CV-OCP measurement sequence described above was performed after each of twenty additions of 10.0 μL analyte solution, affording analyte concentrations ranging from 0.025 to 0.40 M. Data are shown in Supporting Information Figure S4A.

OCP vs $Fc^{+/0}$ as a Function of $[Et_3N^-]$ with No Added Acid. A 1.0 mL portin of the above electrolyte solution was transferred to a new vial and sparged with hydrogen and one crystal of ferrocene was added. The CV-OCP measurement sequence described above was performed after each of ten additions of 1.0 μL Et_3N, and after each of ten additions of 10.0 μL Et_3N, affording analyte concentrations ranging from 0.0072 to 0.70 M. Data are shown in Supporting Information Figure S4B.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1-S5 as mentioned in the text and aggregation refinement models. Data and graphs presented in Excel format. 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.

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