Article

Standard Reduction Potentials for Oxygen and Carbon Dioxide Couples in Acetonitrile and N,N-Dimethylformamide

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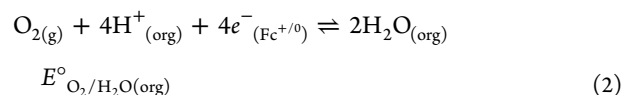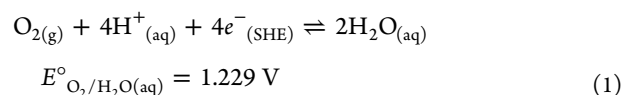
S *Supporting Information*

ABSTRACT: A variety of next-generation energy processes utilize the electrochemical interconversions of dioxygen and water as the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Reported here are the first estimates of the standard reduction potential of the $O_2 + 4e^- + 4H^+ \rightleftharpoons 2H_2O$ couple in organic solvents. The values are +1.21 V in acetonitrile (MeCN) and +0.60 V in N,N-dimethylformamide (DMF), each versus the ferrocenium/ferrocene couple ($Fc^{+/0}$) in the respective solvent (as are all of the potentials reported here). The potentials have been determined using a thermochemical cycle that combines the free energy for transferring water from aqueous solution to organic solvent, -0.43 kcal mol^{-1} for MeCN and -1.47 kcal mol^{-1} for DMF, and the potential of the H^+/H_2 couple, -0.028 V in MeCN and -0.662 V in DMF. The H^+/H_2 couple in DMF has been directly measured electrochemically using the previously reported procedure for the MeCN value. The thermochemical approach used for the O_2/H_2O couple has been extended to the CO_2/CO and CO_2/CH_4 couples to give values of -0.12 and $+0.15$ V in MeCN and -0.73 and -0.48 V in DMF, respectively. Extensions to other reduction potentials are discussed. Additionally, the free energy for transfer of protons from water to organic solvent is estimated as +14 kcal mol^{-1} for acetonitrile and +0.6 kcal mol^{-1} for DMF.

■ INTRODUCTION

The electrocatalytic evolution and reduction of dioxygen are key constituents in many platforms for the interconversion of chemical and electrical energy (eq 1);[1] these reactions are commonly called the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR), respectively. Similarly, there is much current interest in the reduction of CO_2, for instance, to CO.[2] Considerable research efforts are being devoted to developing efficient and low-cost electrocatalysts for these reactions, including both molecular and heterogeneous electrocatalysts. In many cases, these reactions are being studied in organic solvents rather than the more traditional aqueous solutions, for a number of reasons.[3] Organic solvents have larger electrochemical regions of stability, which is useful for the production of fuels and in next-generation energy technologies such as new classes of fuel cells, metal-air batteries, and flow batteries. Organic solvents also dissolve many molecular catalysts and can facilitate mechanistic studies.

$$O_{2(g)} + 4H^+_{(aq)} + 4e^-_{(SHE)} \rightleftharpoons 2H_2O_{(aq)}$$

$$E^\circ_{O_2/H_2O(aq)} = 1.229 \text{ V} \tag{1}$$

$$O_{2(g)} + 4H^+_{(org)} + 4e^-_{(Fc^{+/0})} \rightleftharpoons 2H_2O_{(org)}$$

$$E^\circ_{O_2/H_2O(org)} \tag{2}$$

The efficiency of an electrocatalyst is typically defined as a function of its rate and overpotential, which are interrelated quantities.[4] The overpotential is the difference between the equilibrium potential for the reaction under the reaction conditions, E, and the applied potential. This equilibrium potential is related to the standard potential, E°, via the Nernst equation.

The standard potential of the dioxygen half reaction in water (eq 1) is well-established[5] from both thermochemical

calculations[6] and experimental measurements.[7] The accepted potential is 1.229 V referenced, by convention, to the standard hydrogen electrode (SHE) under the standard conditions of aqueous acid with unit activity (pH 0) and an oxygen pressure of 1 atm.[5,8]

This Article provides estimates of the standard reduction potentials for the O_2/H_2O couple in acetonitrile (MeCN) and *N,N*-dimethylformamide (DMF), eq 2 (org = organic solvent). Our method combines thermochemical cycles and experimental measurements. To our knowledge, these are the first values presented for dioxygen potentials in any nonaqueous solvent. The same approach has been extended to estimate the potentials for the CO_2/CO and CO_2/CH_4 couples. An estimate of a related CO_2/CO couple in these solvents was reported in 2012 using a different approach and an unusual standard state, and a value using a similar approach to ours was published during review of this Article.[9]
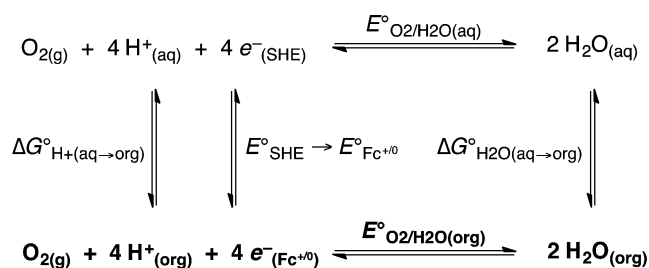
The equilibrium potential for the hydrogen evolution reaction (HER), $2H^+ + 2e^- \rightleftharpoons H_2$, provides a crucial foundation for the evaluation of homogeneous HER electrocatalysts.[10] We also report here the first measurement of the HER standard potential in DMF. This value, and the previous measurement in MeCN, are the basis of the OER/ORR and CO_2 standard potential calculations. These standard potentials allow determination of the operating overpotentials for OER/ORR and CO_2 electrocatalysis in organic solvents. Knowledge of the overpotentials provides a critical metric for the evaluation of O_2 and CO_2 electrocatalysts under diverse operating conditions.

■ APPROACH

The focus of this section is the O_2/H_2O couple; the CO_2 couples are completely analogous, as discussed subsequently and in the Supporting Information. The standard potential for O_2/H_2O in organic solvents is defined by eq 2, in which O_2 is at 1 atm and H^+ and H_2O are at unit activity in the organic solvent (taken here for convenience to be 1 M H^+ and 1 M H_2O). The potentials are referenced to the ferrocenium/ferrocene redox couple in that solvent, $Fc^{+/0}$, as recommended by IUPAC for nonaqueous solvents.[11]

The O_2/H_2O standard potential can be estimated by direct conversion of the aqueous potential, as illustrated in Scheme 1. In
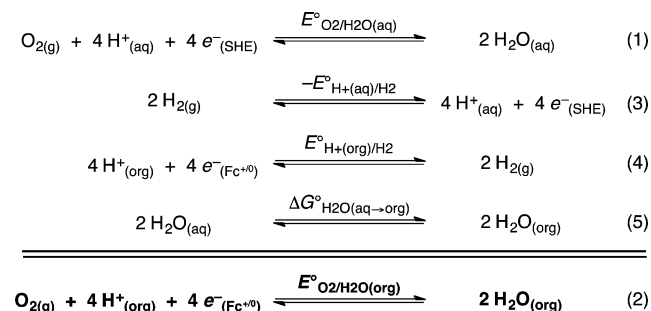
Scheme 1. Thermochemical Cycle To Estimate the Potential of the O_2/H_2O Couple in Organic Solvents

$$O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^-_{(SHE)} \xrightleftharpoons{E^\circ_{O2/H2O(aq)}} 2\,H_2O_{(aq)}$$

$$\Delta G^\circ_{H+(aq\to org)} \quad\quad E^\circ_{SHE} \to E^\circ_{Fc^{+/0}} \quad\quad \Delta G^\circ_{H2O(aq\to org)}$$

$$O_{2(g)} + 4\,H^+_{(org)} + 4\,e^-_{(Fc^{+/0})} \xrightleftharpoons{E^\circ_{O2/H2O(org)}} 2\,H_2O_{(org)}$$

addition to the aqueous O_2/H_2O potential, three parameters are needed: (i) the free energy for transferring a proton from water to organic solvent ($\Delta G_{H^+(aq\to org)}$), (ii) the analogous free energy for transferring water from aqueous solution to organic solvent ($\Delta G_{H_2O(aq\to org)}$), and the potential of the $Fc^{+/0}$ couple in the organic solvent vs SHE. While each of these values has been estimated, the accuracy of these estimates is difficult to assess due to the required extra-thermodynamic assumptions. For instance, published estimates of the free energy for transferring a proton from water to MeCN, $\Delta G_{H^+(aq\to MeCN)}$, have been revised by 5 kcal/mol (0.2 eV) over the evolution of such studies.[12]

To avoid relying on the estimates required for Scheme 1, we have used an alternative approach that utilizes knowledge of the H^+/H_2 standard reduction potentials in both water and the organic solvent (Scheme 2). The couple in water is, of course, defined as having a

Scheme 2. Use of the H^+/H_2 Couples in Water and Organic Solvent To Estimate the O_2/H_2O Couple in Organic Solvent

$$O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^-_{(SHE)} \xrightleftharpoons{E^\circ_{O2/H2O(aq)}} 2\,H_2O_{(aq)} \quad (1)$$

$$2\,H_{2(g)} \xrightleftharpoons{-E^\circ_{H+(aq)/H2}} 4\,H^+_{(aq)} + 4\,e^-_{(SHE)} \quad (3)$$

$$4\,H^+_{(org)} + 4\,e^-_{(Fc^{+/0})} \xrightleftharpoons{E^\circ_{H+(org)/H2}} 2\,H_{2(g)} \quad (4)$$

$$2\,H_2O_{(aq)} \xrightleftharpoons{\Delta G^\circ_{H2O(aq\to org)}} 2\,H_2O_{(org)} \quad (5)$$

$$O_{2(g)} + 4\,H^+_{(org)} + 4\,e^-_{(Fc^{+/0})} \xrightleftharpoons{E^\circ_{O2/H2O(org)}} 2\,H_2O_{(org)} \quad (2)$$

potential of zero (SHE). The H^+/H_2 standard potential in MeCN vs $Fc^{+/0}$ has been determined recently using direct measurements of open-circuit potentials to determine equilibrium potentials, which were extrapolated to standard-state conditions.[13] The extension of that work to give the H^+/H_2 standard potential in DMF is described below.

In essence, the approach in Scheme 2 uses the measured hydrogen couples to avoid two significant estimations in Scheme 1: the free energy for moving H^+ from water to organic solvent and the difference in the potential scales, SHE vs $Fc^{+/0}$. The standard states of O_2 and H_2 (and all gases) are as gases at partial pressures of 1 atm. Therefore, there is no need to correct for the differences in solubility of the gases between the two solvents. The standard states for O_2 and H_2 are the same in all of the equations.

The last term needed in Scheme 2 (eq 5) is the free energy for transferring water from aqueous solution into the organic solvent, $\Delta G^\circ_{H_2O(aq\to org)}$. It also appears on the right side of Scheme 1. While this term should not be ignored, it is a relatively small contributor to the overall potential, as shown below.

The approach described herein also enables estimation of other standard potentials in MeCN and DMF based on the aqueous values. For instance, the reduction of CO_2 to CO requires exactly the same terms: the aqueous potential and eqs 3−5 in Scheme 2.

■ RESULTS AND DISCUSSION

H^+/H_2 Equilibrium Potential in DMF. We have determined the H^+/H_2 standard potential in DMF by extending our recently reported procedure[13] for this potential in MeCN (Figure 1). This procedure uses the open-circuit potential at a freshly cleaned platinum wire as a function of acid
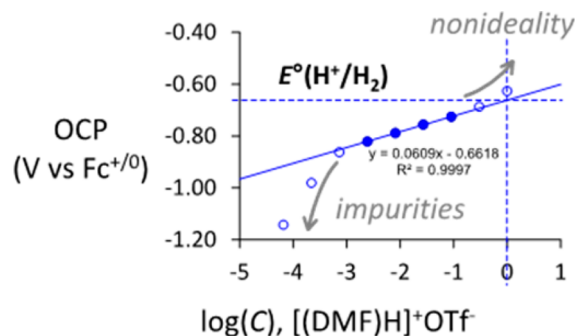
Figure 1. Open-circuit potential (OCP) measurements for H^+/H_2 in DMF under 1 atm H_2 in the presence of various concentrations of $[(DMF)H]^+OTf^-$.

**Table 1. Standard Reduction Potentials (V) in Water, MeCN, and DMF[a]**

reaction	$E°$ in H_2O (vs SHE)	$E°$ in MeCN (vs $Fc^{+/0}$)	$E°$ in DMF (vs $Fc^{+/0}$)
$2H^+_{(solv)} + 2e^- \leftrightarrows H_{2(g)}$	0	-0.028^b	-0.662
$O_{2(g)} + 4e^- + 4H^+_{(solv)} \leftrightarrows 2H_2O_{(solv)}$	$+1.229^c$	$+1.21$	$+0.60$
$O_{2(g)} + 4e^- + 4HA_{(solv)} \leftrightarrows 2H_2O_{(solv)} + 4A^-_{(solv)}$	$+1.229 - 0.0592$ pH	$+1.21 - 0.0592$ $pK_{a(HA)}$	$+0.60 - 0.0592$ $pK_{a(HA)}$
$O_{2(g)} + 2H_{2(g)} \leftrightarrows 2H_2O_{(solv)}^d$	$+1.229^d$	$+1.24^d$	$+1.26^d$
$CO_{2(g)} + 2e^- + 2H^+_{(solv)} \leftrightarrows CO_{(g)} + H_2O_{(solv)}$	-0.104^c	-0.12	-0.73
$CO_{2(g)} + 8e^- + 8H^+_{(solv)} \leftrightarrows CH_{4(g)} + 2H_2O_{(solv)}$	$+0.169^c$	$+0.15$	-0.48

[a]Values are estimated standard reduction potentials $E°$ and are from this work, unless otherwise noted. solv = solvent; SHE = standard hydrogen electrode (aqueous); $Fc^{+/0}$ = ferrocenium/ferrocene. [b]Ref 13. [c]Ref 5. [d]Cell voltage for the whole (not half) reaction: $\Delta G° = -4FE°$.

concentration. The MeCN measurements used acids with established pK_a values in MeCN, whereas those in DMF were done more simply by measuring the potential as a function of the concentration of protonated-DMF (using isolated[14] $[(DMF)H]^+OTf^-$). Given that the acid used is protonated-DMF, the solvated proton concentration in DMF solution is equivalent to the concentration of added acid. Thereby, the H^+/H_2 potential in DMF can be determined without the need for a pK_a scale to determine the standard-state potential (see the Supporting Information for details).

As shown in Figure 1, ideal Nernstian behavior is observed between 1 and 100 mM $[(DMF)H]^+OTf^-$. At concentrations below 1 mM, impurities in the system affect the measurements. Above 0.1 M $[(DMF)H]^+OTf^-$, the activity of the proton starts to diverge from the nominal concentration, likely due to nonidealities such as ion-pairing. This nonideality is seen in difference between the extrapolated Nernstian line and the measured OCP, as it amounts to 35 mV at 1 M $[(DMF)H]^+OTf^-$. The IUPAC definition of a solution standard state is the hypothetical state where the solution at the standard concentration is exhibiting dilute solution behavior,[15] so the OCP value extrapolated to 1 M is the appropriate value.

The measured potential of the H^+/H_2 couple in DMF, $E°_{H^+(DMF)/H_2}$, is -0.662 V vs $Fc^{+/0}$ (eq 4_{DMF}). This value is in reasonable agreement with a previous estimate of -0.62 V vs $Fc^{+/0}$.[16] This and all of the other thermochemical values used, measured, and derived here are given in Table 1.

$$2H^+_{(DMF)} + 2e^-_{(Fc^{+/0})} \rightleftharpoons H_{2(g)}$$

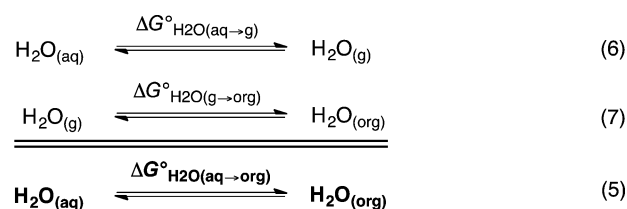$$E°_{H^+(DMF)/H_2} = -0.662 \text{ V} \qquad (4_{DMF})$$
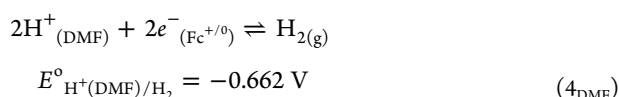
The H^+/H_2 standard potential in DMF is significantly more negative than the analogous potential in MeCN due to the increased basicity of DMF. Comparing the acidities of large series of acids in the two solvents, the pK_a in MeCN has been concluded to be, on average, 10.7 units higher than that in DMF.[17] This difference of 10.7 pK_a units corresponds to a difference in potential of 0.633 V, in excellent agreement with the 0.634 V difference in the H^+/H_2 potentials reported here (Table 1). This close agreement with published pK_a scales provides independent support for our directly measured H^+/H_2 potential in DMF.

Attempts were made to use the same procedure to directly measure the O_2/H_2O standard potential. However, open-circuit measurements were not reproducible and did not follow a simple Nernstian dependence on acid concentration. This difficulty is not surprising given the typical kinetic limitations of the O_2/H_2O couple.[1]

Free Energies for Transfer of H_2O from Water to MeCN or DMF. The free energy for transferring water from

aqueous solution into the organic solvent, $\Delta G°_{H_2O(aq\rightarrow org)}$ (Scheme 2, eq 5), is challenging to measure directly because of the miscibility of water with MeCN or DMF. However, this value can be closely estimated by using the relative vapor pressure of water over pure water versus water over 1 M water in MeCN or DMF, as illustrated in Scheme 3. The vapor

Scheme 3. Free Energy for Transferring Water from Aqueous Solution to MeCN or DMF

$$H_2O_{(aq)} \xrightleftharpoons{\Delta G°_{H2O(aq\rightarrow g)}} H_2O_{(g)} \qquad (6)$$

$$H_2O_{(g)} \xrightleftharpoons{\Delta G°_{H2O(g\rightarrow org)}} H_2O_{(org)} \qquad (7)$$

$$H_2O_{(aq)} \xrightleftharpoons{\Delta G°_{H2O(aq\rightarrow org)}} H_2O_{(org)} \qquad (5)$$

pressure as a function of water concentration has been previously reported for both MeCN[18] and DMF.[19] By comparison to the vapor pressure of pure water, the free energy for transferring water from water to 1 M water in MeCN or DMF was estimated. The derived values are -0.43 kcal mol^{-1} for MeCN[20] and -1.47 kcal mol^{-1} for DMF[21] (Table 2). As noted above, these are small contributors to the overall standard potential.

Table 2. Free Energies for Transfer from Water to Organic Solvents

reaction	$\Delta G°$ to MeCN (kcal/mol)	$\Delta G°$ to DMF (kcal/mol)
$H_2O_{(aq)} \leftrightarrows H_2O_{(org)}$	-0.43	-1.47
$H^+_{(aq)} \leftrightarrows H^+_{(org)}{}^a$	$+14.1^a$	$+0.6^a$

[a]Based on the H^+/H_2 couple in each solvent and the potential of the $Fc^{+/0}_{(org)}$ couple vs SHE in water (taken as $+0.64$ V in MeCN and $+0.69$ V in DMF; see text and Scheme 5).

O_2/H_2O Standard Potentials. The potentials for the O_2/H_2O couples in MeCN and DMF were estimated using the approach in Scheme 2 and the data in Tables 1 and 2. For details of the calculations, see the Supporting Information. The resulting values are $E°_{O_2/H_2O(MeCN)} = +1.21$ V in MeCN and $E°_{O_2/H_2O(DMF)} = +0.60$ V in DMF, vs the $Fc^{+/0}$ couple in each solvent.
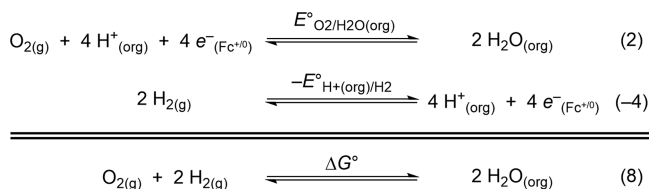
The difference between MeCN and DMF is largely due to the higher basicity of DMF, as indicated by the free energies for H^+ transfer discussed below. The similarity of the value in MeCN ($+1.21$ V) with that in water ($+1.229$ V) is coincidental, resulting from the H^+/H_2 standard potential being defined as

zero in water and being numerically close to the Fc$^{+/0}$ couple in MeCN (−0.028 V).[13]

The sum of eqs 2 and −4 gives eq 8, the free energy of the water splitting reaction (written as the reverse reaction in Scheme 4). $\Delta G°_8 = -114$ kcal mol^{-1} in MeCN and −116 kcal

Scheme 4. Free Energy of O$_2$ + 2 H$_2$ → 2 H$_2$O$_{(org)}$ in MeCN or DMF

$$O_{2(g)} + 4\ H^+_{(org)} + 4\ e^-_{(Fc^{+/0})} \xrightleftharpoons{\ E°_{O2/H2O(org)}\ } 2\ H_2O_{(org)} \qquad (2)$$

$$2\ H_{2(g)} \xrightleftharpoons{\ -E°_{H+(org)/H2}\ } 4\ H^+_{(org)} + 4\ e^-_{(Fc^{+/0})} \qquad (-4)$$

$$O_{2(g)} + 2\ H_{2(g)} \xrightleftharpoons{\ \Delta G°\ } 2\ H_2O_{(org)} \qquad (8)$$

mol^{-1} in DMF, corresponding to full cell potentials of 1.23 and 1.26 V, respectively. These values are very close to those in water (−113.4 kcal mol^{-1} and 1.23 V) because eq 8 in different solvents differs only by the free energy of transfer of H$_2$O from water to the other solvent (eq 5), which is a small value.

It should be emphasized that eq 2 gives the *standard-state* potentials for the specific conditions of 1 M H$^+$, 1 M H$_2$O, and 1 atm O$_2$ at 298 K (actually unit activities of all of these species). For DMF, this standard state is not easily realizable in the laboratory because DMF can hydrolyse to formic acid and NH$_2$Me$_2^+$ under these conditions. In both MeCN and DMF, it is much more typical to use relatively dry solvents. The standard potential can be converted to the equilibrium potential at other concentrations using the Nernst equation (eq 9). This indicates a change of 0.03 V per decade change in water concentration. Thereby, the potential for O$_2$ reduction is 0.09 V higher in a "dry" solvent with H$_2$O ca. = 1 mM.

$$E = E°_{O_2/H_2O(org)}$$
$$- (0.0148\ V)\log\{[H_2O]^2 P(O_2)^{-1}[H^+]^{-4}\} \qquad (9)$$

In acetonitrile, 1 M H$^+$ is difficult to achieve, and typically weak acids and bases are used to deliver and remove the protons. Here, the equilibrium potential can be calculated using the standard-state potential for the O$_2$/H$_2$O couple and the pK_a value of the weak acid, as indicated in eq 10. This equation follows from the Nernst equation (eq 9). We emphasize that for the solution conditions to be consistent with the equilibrium potential provided by eq 10 a 1:1 buffered solution of acid and conjugate base must be used.[22]
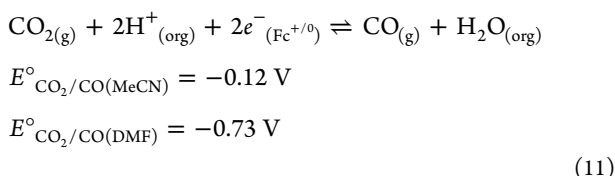
$$E = E° - 0.0592\ pK_a \qquad (10)$$

Additional Considerations. The values reported here are estimates rather than rigorous thermochemical values because some approximations have been made. Some of these approximations are very common, but they still should be mentioned for completeness. Most importantly, some of the above analyses assume ideal solutions, that the activities are equal to the nominal concentrations, and that the solutes and solvent interact equally. This approximation is challenging to avoid in organic solvents and likely introduces an error, especially at high solute concentrations; however, the use of this approximation enables estimation for the thermodynamics potentials proposed herein. We emphasize that this assumption is not used in the measurement of the H$^+$/H$_2$ standard potential, which was extrapolated from low concentrations to the hypothetical unit activity standard state.

Our implementation of Scheme 2 is not strictly correct because our measurements were made under conditions different from the standard-state conditions for the O$_2$/H$_2$O couple. The H$^+$/H$_2$ potential was measured in dry MeCN or DMF, not in solvents containing 1 M H$_2$O. Similarly, the estimates of the free energy of transferring water between solvents were done in the absence of added acid. The primary concern in these cases is that the water and H$^+$ might interact with each other in a nonideal fashion. We had this concern particularly for MeCN solutions since the basicity of pure water is higher than that of acetonitrile.

As a test of how the activity of water changes with the addition of acid, the vapor pressure of water over a solution in acetonitrile was tested with and without 1 M [(DMF)H]$^+$OTf$^-$ (pK_a = 6.1 in MeCN).[23] The presence of added 1 M [(DMF)H]$^+$OTf$^-$ reduced the vapor pressure of water in the gas phase by about a factor of 10, as measured by gas-phase IR spectra (see Supporting Information). An identical experiment with 1:1 ratio of acid/conjugate base (1 M [(DMF)H]$^+$OTf$^-$/1 M DMF) reduced the vapor pressure of water in the gas phase by only a factor of 2. This indicates a change in the activity of the dissolved water by a factor of 2 and suggests a change in the activity of H$^+$ by the same amount. Putting these changes into the Nernst equation (eq 10) predicts a shift in the potential of 0.01 V.[24] That this is a small effect is perhaps not surprising since, in MeCN, H$_3$O$^+$ is orders of magnitude more acidic than [(DMF)H]$^+$OTf$^-$ (the pK_a values are 2.1−2.3 and 6.1, respectively).

In sum, the most critical assumption made in our estimations is ignoring the H$^+$/H$_2$O interaction, especially when applied to highly acidic solutions. We encourage readers to consider this interaction when applying the thermodynamic approach described in Scheme 2 to other systems and quantify the uncertainty in the estimated potentials as described above. In the systems described above, our results suggest that the effects on the O$_2$/H$_2$O potential from proton-water solute/solute interactions are quite minor. These effects are likely smaller than the uncertainties in the overall O$_2$/H$_2$O standard potential and the uncertainties in typical electrocatalysis experiments.

CO$_2$ Potentials. The approach shown for the O$_2$/H$_2$O couple in Scheme 2 can be extended to additional reduction potentials in MeCN or DMF. One example of recent interest is the reduction potential for the CO$_2$/CO couple. Since the aqueous standard potential is known (−0.104 V)[5] and CO$_2$ and CO are gases, no additional parameters are required beyond those in Scheme 2 (see Scheme S1 in the Supporting Information for the analogue of Scheme 2). Using this approach, the standard reduction potential for the CO$_2$/CO couple (eq 11) is estimated to be −0.12 V in MeCN and −0.73 V in DMF. As discussed above, these standard potentials can also be converted to more typical conditions using eqs 9 and 10, with all of the same considerations. The values derived here for eq 11 differ from a previous estimate for the CO$_2$/CO reduction potential, probably because the previous estimates required extra-thermodynamic assumptions.[9a] A similar approach to that in Scheme 2 was published during review of this Article, and the estimated potential for the CO$_2$/CO couple in MeCN is within 10 mV of the value reported herein.[9b]

$$CO_{2(g)} + 2H^+_{(org)} + 2e^-_{(Fc^{+/0})} \rightleftharpoons CO_{(g)} + H_2O_{(org)}$$

$$E^\circ_{CO_2/CO(MeCN)} = -0.12 \text{ V}$$

$$E^\circ_{CO_2/CO(DMF)} = -0.73 \text{ V}$$

<div align="right">(11)</div>

The eight-electron eight-proton reduction of CO_2 to $CH_{4(g)}$ can be analyzed in the same way (Supporting Information Scheme S2), and the derived values are given in Table 1. The common feature of all of the potentials estimated here is that the standard state of all of the reactants and products are gases, except for H^+ and H_2O.
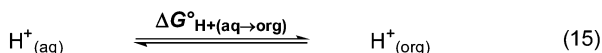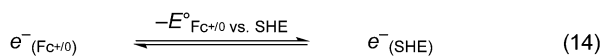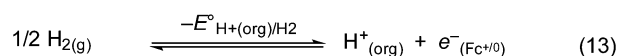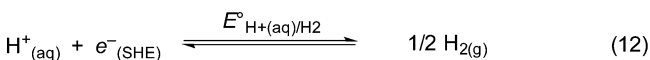
The approach developed here to convert aqueous to organic reduction potentials could also be used for other half-reactions, but additional free energies of solute transfer would be required. For the $6e^-/6H^+$ reduction of CO_2 to methanol in MeCN, for instance, the relevant thermochemical cycle includes the free energy of transfer of methanol from water to MeCN, $\Delta G^\circ_{CH_3OH(aq \to org)}$. Since these changes in solvation terms are not large, we believe that interested readers could use this approach to obtain estimates of such potentials by incorporating limited additional experiments, computations, or assumptions.

Free Energy of Intersolvent Proton Transfer. In addition to determining the potentials for various couples in organic solvents, the data and a variant of the approach described above provide the sum of the free energies for transferring H^+ between aqueous solution and organic solvent and the potential of $Fc^{+/0}$ in organic solvent vs aqueous SHE (Scheme 5). This sum can be used to estimate one value from the other. As an example, the free energy for transferring H^+ between aqueous solution and organic solvents can be determined based on eqs 12 and 13 and the potential of $Fc^{+/0}$ vs SHE.

The free energy of proton transfer, $\Delta G^\circ_{H^+(aq \to org)}$, is a key component in a number of thermochemical cycles, but the proposed values vary substantially.[12] Following Scheme 5,

Scheme 5. Use of H^+/H_2 Potentials To Estimate $\Delta G^\circ_{H^+(aq \to org)}$

$$H^+_{(aq)} + e^-_{(SHE)} \xrightarrow{E^\circ_{H+(aq)/H2}} 1/2\, H_{2(g)} \qquad (12)$$

$$1/2\, H_{2(g)} \xrightarrow{-E^\circ_{H+(org)/H2}} H^+_{(org)} + e^-_{(Fc^{+/0})} \qquad (13)$$

$$e^-_{(Fc^{+/0})} \xrightarrow{-E^\circ_{Fc^{+/0} \text{ vs. SHE}}} e^-_{(SHE)} \qquad (14)$$

$$H^+_{(aq)} \xrightarrow{\Delta G^\circ_{H+(aq \to org)}} H^+_{(org)} \qquad (15)$$

$\Delta G^\circ_{H^+(aq \to org)}$ is derived from the H^+/H_2 potentials in the aqueous and organic media and a term for the potential for the $Fc^{+/0}$ couple in organic solvent versus the SHE in water. Unfortunately, there are also numerous accepted values for the $Fc^{+/0}$/SHE conversion. For example, in MeCN, reported values range from +0.528 to +0.64 V, with the differences likely due to unquantified junction potentials between aqueous and organic solutions.[25] However, the differences in the entire range of values (~0.11 V) is considerably smaller than the range of proposed values for $\Delta G^\circ_{H^+(aq \to org)}$. Using the common values of +0.64 V in MeCN[25] and +0.69 V in DMF[25] for the potentials

of the $Fc^{+/0}$ couple vs SHE, the resulting free energies for transferring H^+ from aqueous solution to organic solvent are estimated as +14.1 kcal mol^{-1} for MeCN and +0.6 kcal mol^{-1} for DMF (Table 2). The large difference between these values is a result of the much higher basicity of DMF, as noted above in another context. The difficulties estimating the thermodynamics of intersolvent proton transfer *and* a reliable conversion between $Fc^{+/0}$/SHE were motivation for avoiding Scheme 1.

■ SUMMARY AND CONCLUSIONS

The standard reduction potential for the O_2/H_2O couple in MeCN and DMF has been estimated to be +1.21 and +0.60 V, respectively, each versus the ferrocenium/ferrocene couple ($Fc^{+/0}$) in the same solvent (Table 1). To our knowledge, these are the first estimates of these O_2 reduction potentials in organic solvents. Similarly, values for the CO_2/CO and CO_2/CH_4 couples are reported in these solvents, −0.12 and +0.15 V in MeCN and −0.73 and −0.48 V in DMF (vs $Fc^{+/0}$), respectively. These values are based on experimental measurements of the potential for the H^+/H_2 couple, the free energy for transferring water from aqueous solution to respective organic solvents (Table 2), and the known aqueous standard potentials. The potential of the H^+/H_2 couple in DMF was directly determined experimentally to be −0.662 V vs $Fc^{+/0}$, based on open-circuit potential measurements as a function of protonated-DMF concentration. This avoids the need for a DMF pK_a scale to define the standard potential (though the DMF pK_a scale is needed for other acids). Additionally, this approach enables the estimation of the free energy of transferring a proton from water to MeCN and DMF as +14 and +0.6 kcal mol^{-1}, respectively.

There are many current research efforts on O_2 and CO_2 reduction in organic solvents. The thermodynamic potentials reported here, that have not been previously available, are a critical benchmark against which the operating potentials of these catalysts should be measured.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02136.

> Additional experimental details and thermodynamic calculations (PDF)

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Author Contributions

All authors have contributed to the ideas and writing of the manuscript, and all have given approval to the final version of the manuscript. The measurement of the potential of the H^+/H_2 couple in DMF was done by JASR; other experiments were done by JASR, DJW and MLP.

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