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Electronic Supplementary Information for:

Predicting the Reactivity of Hydride Donors in Water: Thermodynamic Constants for Hydrogen

Dalton Transactions **Perspective**

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NHE vs SHE

The difference in potential between the Normal Hydrogen Electrode (NHE) and the Standard Hydrogen Electrode (SHE) is 0.006 V,[1,2] which stems from using 1 N solvated H^+ vs unit activity of solvated H^+. We have adopted and recommend NHE based on the lack of activity coefficients to describe H^-. The small difference in potential between NHE and SHE translates to ~ 0.3 kcal/mol. Therefore, the difference is easily within the typical experimental error of the thermodynamic data for which the constants are used.

Interconversion of Units and Expressions.

Free energies in kcal/mol ($\Delta G°$), equilibrium constants (K), and electrochemical reduction potentials ($E°$) can all be interconverted using eqs S1-S2.

$$\Delta G° = -RT \ln K \tag{S1}$$

$$\Delta G° = -nFE° \tag{S2}$$

At 25 °C for a one-electron process (n=1), eqs S1-S2 can be written as eqs S3-S4.

$$\Delta G° = -1.364 \log(K) \tag{S3}$$

$$\Delta G° = -23.06\ E° \tag{S4}$$

The conversions for moving from eq S1 to S3 include RT expressed in kcal/mol and the conversion from natural log to log base 10 ($\log_{10}$), which is accomplished diving $\ln(K)$ by $\log_{10}(e)$. Similarly, the conversion from eq S2 to S4 is accomplished by expressing nF in kcal mol^{-1} V^{-1}, for a one-electron process. The analogous expression for a two-electron process contains –46.12 $E°$. A special case of eq S3 is that of pK_a values, for which S3 and S5 lead to S6.

$$\mathrm{p}K_a = -\log(K_a) \tag{S5}$$

$$\Delta G° = +1.364\ \mathrm{p}K_a \tag{S6}$$

Determining the pH at which a Reaction Becomes Thermoneutral.

One extension of the use of eq S6 is the prediction of the pH at which a reaction that includes a proton is thermoneutral. Eq 17 in the main text describes the extent to which hydrogenation of CO_2 to formate is unfavorable under standard state conditions. At the 1 M standard state for H^+ (pH = 0), the free energy of the (standard state) reaction is +10.1 kcal/mol. Using eq S7, this free energy can be converted to the pH at which eq 17 becomes thermoneutral.

$$\mathrm{pH} = \log\left(\frac{[\mathrm{HCO_2}^-]}{\mathrm{P_{CO_2}P_{H_2}}}\right) - \log\left(K_{\mathrm{eqn\_17}}\right) = \log\left(\frac{[\mathrm{HCO_2}^-]}{\mathrm{P_{CO_2}P_{H_2}}}\right) + \frac{\Delta G_{\mathrm{eqn\_17}}}{1.364} \qquad \text{(S7)}$$

At 1 M HCO_2^-, and 1 atm each of CO_2 and H_2, the first term is zero, leaving the standard state reaction free energy of eq 17 divided by 1.364 (to convert from a value in kcal/mol derived from using $-RT \ln K$). The resulting pH value is 7.4.

Similarly, the equilibrium for the formation of a metal-hydride can be determined by dividing the equilibrium expression for heterolytic cleavage of H_2 (eqn 6) by the hydricity expression (K_{H-}), as shown in eqn S8. In turn, this expression can be rearranged to eqn S9 to determine the pH at which the hydride becomes stable (or the pH above which formation of the hydride from H_2 is favorable).

$$\frac{K_{\mathrm{eqn\_6}}}{K_{\mathrm{H^-}}} = \frac{\left(\frac{[\mathrm{H^-}][\mathrm{H^+}]}{\mathrm{P_{H_2}}}\right)}{\left(\frac{[\mathrm{M^+}][\mathrm{H^-}]}{[\mathrm{M{-}H}]}\right)} = \left(\frac{[\mathrm{M{-}H}][\mathrm{H^+}]}{[\mathrm{M^+}]\mathrm{P_{H_2}}}\right) \qquad \text{(S8)}$$

$$\mathrm{pH} = \log\left(\frac{[\mathrm{M{-}H}]}{[\mathrm{M^+}]\mathrm{P_{H_2}}}\right) - \log\left(K_{\mathrm{eqn}_6}\right) + \log\left(K_{\mathrm{H^-}}\right) = \log\left(\frac{[\mathrm{M{-}H}]}{[\mathrm{M^+}]\mathrm{P_{H_2}}}\right) + \frac{34.2}{1.364} - \frac{\Delta G_{\mathrm{H^-}}}{1.364} \qquad \text{(S9)}$$

For a 1:1 ratio of M-H and M^+ at 1 atm of H_2, the expression simplifies to the difference between the heterolytic cleavage free energy for H_2 and the hydricity of M-H, each divided by 1.364 (to convert from a value in kcal/mol derived from using $-RT \ln K$).

Source of Self-Consistent Constants.

The values shown in Scheme 1 of the main text were determined starting from the definition of the Normal Hydrogen Electrode (NHE) (eq 1). This defines the potential for the reaction between two solvated, aqueous protons and two electrons to produce hydrogen gas at 1 atm and pH = 0 to be 0 V. All calculations below were converted to kcal/mol.

The following gas phase formation constants are those calculated from the reported enthalpies and entropies of formation in the NIST Chemistry WebBook.[3]

Species	**$\Delta H_f°$ (kJ/mol)**	**$S_f°$ (J/mol*K)**	**$\Delta G_f°$ (298.15 K) (kJ/mol)**	**$\Delta G_f°$ (298.15 K) (kcal/mol)**
$H_{2(g)}$	0	130.680	– 38.962	-9.312
$H^{\bullet}_{(g)}$	217.999	114.716	+ 183.796	43.93
$H^{+}_{(g)}$	1536.246	108.946	+ 1503.764	359.4
$H^{-}_{(g)}$	139.032	108.960	+ 106.546	25.47

The solvation (hydration) of each of these species have been measured or estimated:

Species	$\Delta G_{solv}°$ (298.15 K) (kJ/mol)	$\Delta G_{solv}°$ (298.15 K) (kcal/mol)
$H_{2(g\rightarrow aq)}$		+ 4.25
$H^{\bullet}_{(g\rightarrow aq)}$		+ 4.25
$H^{+}_{(g\rightarrow aq)}$	– 1104	– 263.9
$H^{-}_{(g\rightarrow aq)}$	– 402	– 96.1

$\Delta G_{solv}°$ (H_2) is calculated using Eq S1 and the appropriate Henry's Law constant.

K_H = 0.00078 M/atm;[4]

$\Delta G° = -RT \ln K$, where $K = K_H$

$= -$ (0.0019872 kcal/mol*K)(298.15 K) ln (0.00078 M/atm)

$= +$ 4.25 kcal/mol

The solvation of $H^{\bullet}$ has been estimated to be nearly equivalent to that of H_2.[5] The solvation energy of a proton can be extrapolated from gas-phase ion cluster data.[6] The table below lists the data used by Kelly and Rosseinsky[7] for determination of the solvation energy of a hydride, as well as the value obtained by using the updated data for the halides tabulated by Fawcett.[8]

Species	**Radius** [a]	**ΔG°_{solv} old (kJ/mol)** [a]	**ΔG°_{solv} updated (kJ/mol)** [b]	**ΔG°_{solv} updated (kcal/mol)** [b]
H^+	--	1088	1104	263.9
I^-	2.20	259	243	58.1
Br^-	1.96	305	278	66.4
Cl^-	1.81	319	304	72.7
F^-	1.33	436	429	103
H^-	1.38	421 [c]	402 [c]	96.1

[a] Tabulated by Kelly and Rosseinsky.[7] [b] Tabulated by Fawcett.[8] [c] Determined from a plot of ΔG°_{solv} versus 1/r for the halide series (Kelly and Rosseinsky's method).[7]

Determining the Thermodynamic Constants

(Equation 2) **$H_2\,(g) \rightarrow 2\,H^{\bullet}\,(aq)$**

Thermochemical Cycle:

Reaction a:	$H_2\,(g) \rightarrow 2\,H^{\bullet}\,(g)$	+ 97.17	kcal/mol
Reaction b:	$2\,H^{\bullet}\,(g) \rightarrow 2\,H^{\bullet}\,(aq)$	+ 8.50	kcal/mol
Main Text Equation 2:	**$H_2\,(g) \rightarrow 2\,H^{\bullet}\,(aq)$**	**+ 105.67**	**kcal/mol**

Reaction a:

$$\begin{aligned}\Delta G_{rxn} &= [2 \text{ x } \Delta G_f\,(H^{\bullet}\,(g))] - [\Delta G_f\,(H_2\,(g))]\\ &= [2 \text{ x } 43.93 \text{ kcal/mol}] - [-9.312 \text{ kcal/mol}]\\ &= 97.17 \text{ kcal/mol}\end{aligned}$$

Reaction b:

$$\begin{aligned}\Delta G_{rxn} &= [2 \text{ x } \Delta G_{solv}\,H^{\bullet}\,(g \rightarrow aq)]\\ &= [2 \text{ x } 4.25 \text{ kcal/mol}]\\ &= 8.50 \text{ kcal/mol}\end{aligned}$$

(Equation 3) **$H^+\,(aq) + e^- \rightarrow H^{\bullet}\,(aq)$**

Thermochemical Cycle:

Reaction a:	$2\,H^+\,(aq) + 2\,e^- \rightarrow H_2\,(g)$	+ 0.00	kcal/mol
Reaction b:	$H_2\,(g) \rightarrow 2\,H^{\bullet}\,(aq)$	+ 105.67	kcal/mol
2 x Main Text Equation 3:	$2\,H^+\,(aq) + 2\,e^- \rightarrow 2\,H^{\bullet}\,(aq)$	+ 105.67	kcal/mol
Main Text Equation 3:	**$H^+\,(aq) + e^- \rightarrow H^{\bullet}\,(aq)$**	**+ 52.835**	**kcal/mol**

Reaction a: ΔG_{rxn} = 0.00 kcal/mol (Definition of NHE)

Reaction b: ΔG_{rxn} = 105.67 kcal/mol (Main Text Eq. 2)

(Equation 4) **$H^{\bullet}\,(aq) + e^{-} \rightarrow H^{-}\,(aq)$**

Thermochemical Cycle:

Reaction a:	$2\,H^{+}\,(aq) + 2\,e^{-} \rightarrow H_2\,(g)$	+ 0.00	kcal/mol
Reaction b:	$H^{\bullet}\,(aq) \rightarrow H^{+}\,(aq) + e^{-}$	– 52.835	kcal/mol
Reaction c:	$H_2\,(g) \rightarrow H^{+}\,(aq) + H^{-}\,(aq)$	+ 34.2	kcal/mol
Main Text Equation 4:	**$H^{\bullet}\,(aq) + e^{-} \rightarrow H^{-}\,(aq)$**	**– 18.6**	**kcal/mol**

Reaction a: ΔG_{rxn}= 0.00 kcal/mol (Definition of NHE)

Reaction b: ΔG_{rxn}= –52.835 kcal/mol (Reverse of Main Text Eq. 3)

Reaction c: ΔG_{rxn}= + 34.2 kcal/mol (Main Text Eq. 6)

(Equation 5) **$H^{+}\,(aq) + 2\,e^{-} \rightarrow H^{-}\,(aq)$**

Thermochemical Cycle:

Reaction a:	$2\,H^{+}\,(aq) + 2\,e^{-} \rightarrow H_2\,(g)$	+ 0.00	kcal/mol
Reaction b:	$H_2\,(g) \rightarrow H^{+}\,(aq) + H^{-}\,(aq)$	+ 34.2	kcal/mol
Main Text Equation 5:	**$H^{+}\,(aq) + 2\,e^{-} \rightarrow H^{-}\,(aq)$**	**+ 34.2**	**kcal/mol**

Reaction a: ΔG_{rxn}= 0.00 kcal/mol (Definition of NHE)

Reaction b: ΔG_{rxn}= +34.2 kcal/mol (Main Text Eq. 6)

(Equation 6) **$H_2\,(g) \rightarrow H^+\,(aq) + H^-\,(aq)$**

Thermochemical Cycle:

Reaction a:	$H_2\,(g) \rightarrow H^+\,(g) + H^-\,(g)$	+ 394.2	kcal/mol
Reaction b:	$H^+\,(g) \rightarrow H^+\,(aq)$	– 263.9	kcal/mol
Reaction c:	$H^-\,(g) \rightarrow H^-\,(aq)$	– 96.1	kcal/mol
Main Text Equation 6:	**$H_2\,(g) \rightarrow H^+\,(aq) + H^-\,(aq)$**	**+ 34.2**	**kcal/mol**

Reaction a:

$$
\begin{aligned}
\Delta G_{rxn} &= [\,\Delta G_f\,(H^+\,(g)) + \Delta G_f\,(H^-\,(g))] - [\,\Delta G_f\,(H_2\,(g))] \\
&= [359.4 + 25.47 \text{ kcal/mol}] - [-\,9.312 \text{ kcal/mol}] \\
&= 394.2 \text{ kcal/mol}
\end{aligned}
$$

Reaction b: $\Delta G_{solv} = -\,263.9$ kcal/mol (From Table ESI pg. 5)

Reaction b: $\Delta G_{solv} = -\,96.1$ kcal/mol (From Table ESI pg. 5)

Choice of Standard State for Gases

Concentration vs Pressure. Standard states for gases can be expressed as either gas pressures (1 atm standard state) or solute concentrations (1 M standard state). Either convention, if used consistently, can be used to determine thermodynamic values. However, a concentration of 1 M for dissolved gases is not typically experimentally achievable due to the low solubility of most gases. Therefore, predicting reactivity from equilibrium constants and free energies of reaction is less obvious using a 1 M standard state for gases. The difference between the two standard state conventions (1 M gases vs 1 atm gases) is the Henry's Law constant (K_H) for the specific gas, which can be converted to a reaction free energy using eq S3. For a simple reaction of H_2 with an inorganic complex (M^+), the difference in the standard state free energies using the two different conventions is illustrated using eqs S10-S12 for H_2, for which K_H is 7.8×10^{-4} M/atm.[9] For this example, eq S10 is arbitrarily defined as thermoneutral to illustrate the difference in free energies for the same reaction using the two different standard state conventions.

$$\begin{array}{llrr}
\mathrm{M^{+}_{(aq)} + H_{2(g)} \rightleftharpoons M(H_2)^{+}_{(aq)}} & & 0\ \text{kcal/mol} & \text{(S10)} \\
\mathrm{H_{2(aq)} \rightleftharpoons H_{2(g)}} & (1/K_\mathrm{H}) & -4.25\ \text{kcal/mol} & \text{(S11)} \\
\hline
\mathrm{M^{+}_{(aq)} + H_{2(aq)} \rightleftharpoons M(H_2)^{+}_{(aq)}} & & -4.25\ \text{kcal/mol} & \text{(S12)}
\end{array}$$

Effects of Ambient Pressure. While changes in pressure will affect the free energies of reactions that include gases, the effect of the change due to differences in elevation or barometric pressure are relatively small when expressed in kcal/mol. For example, the difference between the average pressure at sea level (1.0 atm) and in Denver, CO (0.83 atm) is –1.364 log (0.83), or 0.11 kcal/mol. While the difference in pressure should be considered for precise thermodynamic measurements, the effect on predicting reactivity is essentially negligible for any typical laboratory conditions.

Effects of Gas Mixtures. While standard states are expressed for each individual component (1 atm of pressure for each gas), a reaction that includes multiple gases will have a modest effect based on the mixing of the gases to a total pressure. For example, if a 1:1 mixture of CO_2 and H_2 is used for CO_2 hydrogenation (as is applicable for eq 17 in the main text), then at 1.0 atm total pressure, each gas would have a partial pressure of 0.5 atm. This difference in pressure will have an effect upon the free energy of reaction, but even for a reaction with two gases, the total effect is only 0.8 kcal/mol based on eq S3: $-1.364 \log (0.5^2)$.

Literature Values for Hydricities

Very few studies have been carried out on the hydricity of metal hydride complexes in water. In 2012, Creutz and co-workers demonstrated that hydricities do not scale linearly between acetonitrile and water, so determining the hydricity values in aqueous solution is imperative. In the main text of the paper, Table 1 gives corrected hydricity values for the known species. Below are the relevant calculations and conversions.

Table 1 from Main Text: Hydricities for Reported Water-Soluble Metal Hydride Complexes Based on the Proposed Thermodynamic Constant

Complex[a]	**ΔG_{H-} (kcal/mol)**	**ΔG_{H-} (kJ/mol)**	**Reference**
$[Ru(tpy)(bpy)H]^+$	13.8	58	*JACS* **2009**, *131*, 2794.[10]
$[Ru(\eta^6\text{-}C_6Me_6)(bpy)H]^+$	22.2	93	*JACS* **2009**, *131*, 2794.[10]
$[Ir(TMPS)D(D_2O)]^{8-}$	27.9[b]	117[b]	*Inorg. Chem.* **2011**, *50*, 11011.[11]
$[Rh(TMPS)D(D_2O)]^{8-}$	29.3[b]	123[b]	*Inorg. Chem.* **2006**, *45*, 9884.[12]
$[Rh(TSPP)D(D_2O)]^{4-}$	29.3[b]	123[b]	*JACS* **2004**, *126*, 2623.[13]
$[Rh(bpy)_2(H_2O)H]^{2+}$	41.4	173	(a) *Inorg. Chem.* **1982**, *21*, 3989.[14] (b) *Inorg. Chem.* **1983**, *22*, 707.[15]

Conversion of Previous Values to Current Recommendations

Work from the Wayland Group:

Hydricities were measured using Method 2 described in the Main Text. K_{eq} for the following reaction is reported for each metal complex:

$$[M^{III}(D_2O)_2]^{n-} + D_2 \rightleftharpoons [M^{III}D(D_2O)]^{(n+1)-} + D^+ + D_2O$$

$$K_{eq} = [M^{III}D(D_2O)^{(n+1)-}][D^+][D_2O]/[M^{III}(D_2O)_2{}^{n-}][D_2]$$

Wayland reports that each K_{eq} value includes all constituents (including water and D_2) as concentrations. To convert to our recommended scale, we divided by the molarity of pure D_2O (55.22 M), and included the appropriate Henry's Law constant (K_H (H_2) = 0.00078 M/atm). The free energy of reaction is given in kcal/mol for the reaction as drawn above.

Species	K_{eq} (reported)	K_{eq} (excluding D_2O)	K_{eq} (1 atm H_2)	ΔG_{rxn} (kcal/mol)
$[Rh(TMPS)(D_2O)_2]^{7-}$	18.2	0.330	2.57×10^{-4}	4.90
$[Rh(TSPP)(D_2O)_2]^{3-}$	18.2	0.330	2.57×10^{-4}	4.90
$[Ir(TMPS)(D_2O)_2]^{7-}$	1.7	0.031	2.40×10^{-5}	6.30

Per Method 2 described in the main text, we considered the reverse of the reaction shown, multiplied by $[D^+]$ = 1 M (pH = 0), and added the value of Eq. 6 to generate the hydricity. Because these values are based on deuterated K_{eq} values, the calculated hydricity is only approximate (the "deutericity" could be determined if the heterolytic cleavage free energy for D_2 in water was used in place of the value for Eq 6.)

Species	$-\Delta G_{rxn}$ (kcal/mol)	ΔG_{H-} (kcal/mol)
$[Rh(TMPS)(D_2O)D]^{8-}$	– 4.90	29.3
$[Rh(TSPP)(D_2O)D]^{4-}$	– 4.90	29.3
$[Ir(TMPS)(D_2O)D]^{8-}$	– 6.30	27.9

Work from Cruetz & Co-workers:

Hydricities were measured based on Method 3 described in the Main Text. K_{eq} for the following reaction is reported for the Ru complexes (based on kinetic measurements of the forward and reverse reactions):

$$[Ru^{II}(H_2O)]^{2+} + [HCO_2]^- \rightleftharpoons [Ru^{II}H]^+ + CO_2$$

$$K_{eq} = [Ru^{II}H^+][CO_2]/[Ru^{II}(H_2O)^{2+}][HCO_2^-]$$

As we did above, we converted the concentration of the gas to the pressure using the appropriate Henry's Law constant ($K_H(CO_2) = 3.4 \times 10^{-2}$ M/atm). The free energy of reaction is given in kcal/mol for the reaction as drawn above.

Species	***K*~eq~ (reported)**	***K*~eq~ (1 atm CO~2~)**	**ΔG~rxn~ (kcal/mol)**
$[Ru(tpy)(bpy)H]^+$	$0.9x10^{-9}$	$2.6x10^{-8}$	10.3
$[Ru(\eta^6\text{-}C_6Me_6)(bpy)H]^+$	$1.4x10^{-3}$	$4.1x10^{-2}$	1.9

Per Method 3, the calculated ΔG_{rxn} for the reverse reaction is added to the hydricity of formate (determined in the Main Text in Eqs 10-13 to be + 24.1 kcal/mol).

Species	**$-\Delta G_{rxn}$ (kcal/mol)**	**ΔG_{H-} (kcal/mol)**
$[Ru(tpy)(bpy)H]^+$	– 10.3	13.8
$[Ru(\eta^6\text{-}C_6Me_6)(bpy)H]^+$	– 1.9	22.2

Earlier work from Creutz & Co-workers:

Hydricities can be calculated using Method 1 of the main text from data presented in M. Chou, C. Creutz, D. Mahajan, N. Sutin, A. P. Zipp *Inorganic Chemistry* **1982**, *21*, 3989-3997 and H. A. Schwarz, C. Creutz *Inorganic Chemistry* **1983**, *22*, 707-713.

Reported pK_a value of $[Rh(bpy)_2(H_2O)H]^{2+}$ in water: 7.3

$\Delta G_{rxn} = 1.364 * pK_a = 9.96$ kcal/mol

Reported 1e^- reduction of $[Rh^{III}(bpy)_2(H_2O)]^{3+}$: – 0.57 V *vs*. SHE = – 0.564 *vs*. NHE

$\Delta G_{III/II} = -nFE = +13.0$ kcal/mol

Reported 1e^- reduction potential of $[Rh^{II}(bpy)_2(H_2O)]^{2+}$: +0.46 V *vs*. SHE = +0.466 *vs*. NHE

$\Delta G_{II/I} = -nFE = -10.7$ kcal/mol

$\Delta G_{III/I} = +2.3$ kcal/mol

Using Method 1, the 2-electron oxidation ($-\Delta G_{III/I}$) is combined with the pK_a of the metal hydride complex, the expression for the Normal Hydrogen Electrode, and the free energy for the heterolytic cleavage of H_2:

(– 2.3 kcal/mol) + (9.96 kcal/mol) + (0.00 kcal/mol) + (34.2 kcal/mol) = 41.9 kcal/mol

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