Electronic Supplementary Information

Thermodynamic and Kinetic Hydricities of Metal-Free Hydrides

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1. Electronic Structure Calculations

All electronic structure calculations were performed using DFT-based methods in the Gaussian 09 software package. The B3LYP exchange-correlation functional was used to obtain energies of hydride species (R-H) and their corresponding hydride acceptors (R^+). The triple-ζ 6-311++G(d,p) basis set including polarization functions on both heavy-atoms and hydrogen was used to correctly describe the anionic nature of the hydride atom. The conductor-like polarizable continuum model (CPCM) was used to describe solvation effects in MeCN and DMSO. Optimization and frequency calculations were performed to ensure that all simulated molecules converged to local minimum energy geometries and to calculate zero-point energies. Vibrational thermal contributions to the enthalpy were used to calculate free energies at 298 K. The free energy differences between R-H and R+ were fit to experimental hydricities, in accordance with Muckerman's approach, to obtain a correlation for hydricity predictions. The B3LYP/6-311++G(d,p)/CPCM level of theory was tested against M06-2X/6-311++G(d,p)/SMD, which, was found to reproduce CCSD(T)/cc-PVTZ[1-3] energies of organic molecules sufficiently well,[4] as shown in Figure S1. Results show that the same correlation can be obtained using both levels of theory for a training set of 11 hydride donors.

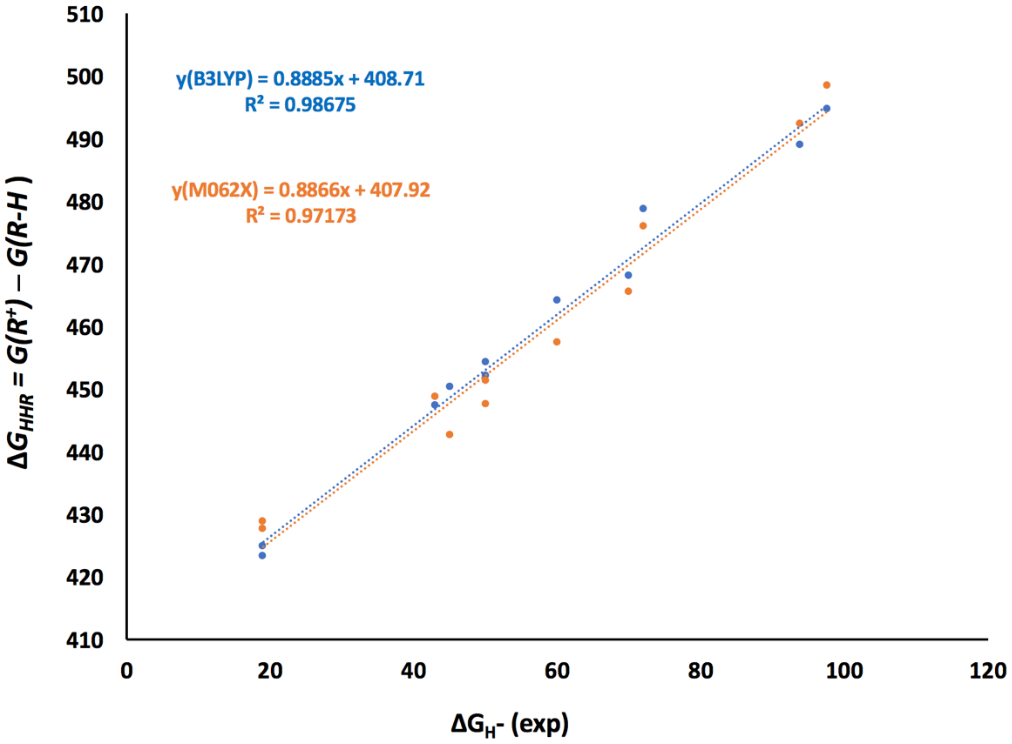


Figure S1. The Gibbs free energy difference $\Delta G_{HHR} = G(R^{+}) - G(R\text{-}H)$ fit against corresponding experimental hydricicities (both in kcal/mol). The B3LYP/6-311++G(d,p)/CPCM (blue) and M06-2X/6-311++G(d,p)/SMD (orange) levels of theory show good agreement in the resulting correlations. Differences in the slopes are minimal (less than 0.002), whereas the y-intercepts are 408.7 (blue) and 407.9 kcal/mol (orange).

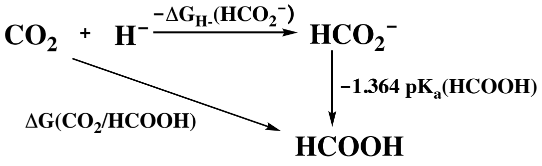
Table S1. Table of experimental (ΔG_{H}-) and calculated (ΔG_{HHR}) values (kcal/mol) presented in Figure S1.

Entry	Solvent	ΔG_{H}-(exp)	ΔG_{HHR}(B3LYP)	ΔG_{HHR}(M062X)
15	MeCN	19	423.3	427.7
16	MeCN	19	424.8	428.9
19	MeCN	43	447.4	448.7
20	MeCN	50	454.2	451.4
21	MeCN	72	478.6	476.0
34	MeCN	97.6	494.6	498.5
35	MeCN	93.9	488.9	492.4
125	MeCN	60	464.2	457.4
170	DMSO	70	468.0	465.5
185	MeCN	45	450.2	442.5
195	MeCN	50.1	452.0	447.6

2. Derivation for ΔG and Reduction Potentials

ΔG(CO_2/HCOOH). The reaction free energy for the proton-coupled hydride transfer to CO_2 (*ΔG(CO_2/HCOOH)*) is determined using the hydride affinity of CO_2 and the pKa of formic acid in acetonitrile (Scheme S1). The hydride affinity is obtained from the hydricity of formate (ΔG_{H-} = 44 kcal/mol[5] in MeCN), whereas the pK_a is derived from the aqueous values (pKa = 21[6] in MeCN). The values obtained for *ΔG(CO_2/HCOOH)* is 72 kcal/mol in MeCN.

Scheme S1. The thermochemical cycle for the determination of *ΔG(CO_2/HCOOH)* using the hydride affinity of CO_2 and the pK_a of formic acid in acetonitrile.



$$\begin{array}{ll} CO_2 + H^- \longrightarrow HCO_2^- & -\Delta G_{H-}(HCO_2^-) \\ HCO_2^- + H^+ \longrightarrow HCOOH & 1.364\ pKa(HCOOH) \\ \hline CO_2 + H^- + H^+ \longrightarrow HCOOH & \Delta G(CO_2/HCOOH) \end{array}$$

Reduction potentials in MeCN. Reduction potentials in MeCN relevant to electrocatalysis ($E(H^+/H_2)$ and $E(CO_2/HCOO^-)$) are derived from thermochemical cycles represented in Scheme S2. The relevant hydricities are $\Delta G_{H^-}(H_2)$ = 76 kcal/mol[7] and $\Delta G_{H^-}(HCOO^-)$ = 44 kcal/mol in MeCN,[5] while the standard reduction potential for the two-electron reduction of a proton is –1.2 V vs. NHE in MeCN.[8] The values obtained for $E(H^+/H_2)$ and $E(CO_2/HCOO^-)$ are 0.46 V and –0.23 V vs. NHE in MeCN.

Scheme S2. Derivation of the reduction potentials ($E(H^+/H_2)$ and $E(CO_2/HCOO^-)$) in MeCN.

(a)

$$\begin{array}{ll}
H^+ + H^- \longrightarrow H_2 & -\Delta G_{H\text{-}}(H_2) \\
H^+ + 2e^- \longrightarrow H^- & -46.12\ E(H^+/H^-) \\
\hline
H^+ + 2e^- + H^+ \longrightarrow H_2 & -46.12\ E(H^+/H_2)
\end{array}$$

(b)

$$\begin{array}{ll}
CO_2 + H^- \longrightarrow HCO_2^- & -\Delta G_{H\text{-}}(HCO_2^-) \\
H^+ + 2e^- \longrightarrow H^- & -46.12\ E(H^+/H^-) \\
\hline
CO_2 + 2e^- + H^+ \longrightarrow HCOO^- & -46.12\ E(CO_2/HCOO^-)
\end{array}$$

3. Bond Dissociation Energies of Metal-Free Hydrides

Bond dissociation energy (BDE) for the bond R-H, the energy for the release of a hydrogen atom, can be obtained from the second reduction potential E_2 of R^+ and the pK_a value of R-H (Scheme S3). The derivation requires two reduction potentials of protons in MeCN[8] (*E(H+/H)* = –1.77 V vs. NHE and $E(H/H^-)$ = –0.60 V vs. NHE).

Scheme S3. Two thermochemical cycles for the determination of ΔG_{H^-} where ΔG_{H^-} can be represented as a function of E_1 and the BDE.

$$\begin{array}{ll}
R^+ + e^- \longrightarrow R\cdot & -23.06E_1 \\
R\cdot + e^- \longrightarrow R^- & -23.06E_2 \\
R^- + H^+ \longrightarrow RH & 1.364pK_a(RH) \\
H^- \longrightarrow H^+ + 2e^- & 46.12E(H^+/H^-) \\
\hline
R^+ + H^- \longrightarrow RH & -\Delta G_{H\text{-}}
\end{array}$$

$$\begin{array}{ll}
R^+ + e^- \longrightarrow R\cdot & -23.06E_1 \\
R\cdot + H\cdot \longrightarrow RH & \text{BDE} \\
H^- \longrightarrow H\cdot + e^- & 23.06E(H/H^-) \\
\hline
R^+ + H^- \longrightarrow RH & -\Delta G_{H\text{-}}
\end{array}$$

$$\Delta G_{H\text{-}} = 23.06E_1 + \overbrace{\overbrace{23.06E_2 + 1.364pK_a - 23.06\ E(H^+/H)}^{\text{BDE}} - 23.06\ E(H/H^-)}^{\textit{intercept}}$$

The scaling relationship for metal-free hydrides between ΔG_{H^-} and the first reduction potential E_1 (Figure 6 in the main text) indicate that BDEs are constant across all groups of donors. Indeed, BDE energies derived using Scheme S3 show values of ~75 kcal/mol (Figure S2), which is predicted by the intercept of the linear correlation shown in Figure 6. As shown in Scheme S3, the intercept consists of BDE values and the first reduction potential E_1 of the proton ($E(H/H^-)$).

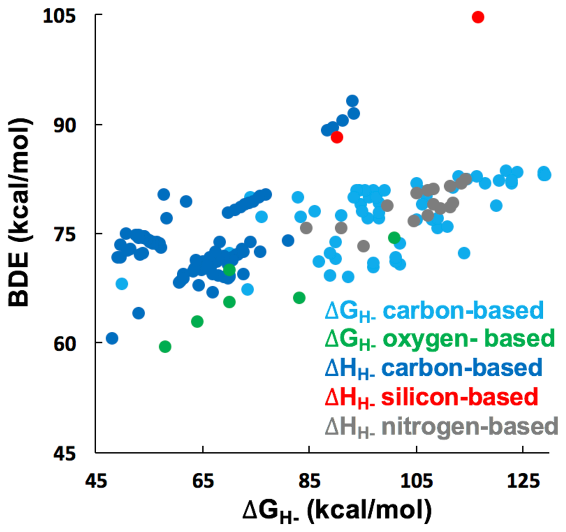


Figure S2. Bond dissociation energy (BDE) as a function of the corresponding ΔG_{H-} for different hydride donor groups.

4. References

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