Electronic Supplementary Information for Determining overpotentials for the oxidation of alcohols by molecular catalysts in non-aqueous solvents

Amy L. Speelman,^a James B. Gerken,^b Spencer P. Heins,^a Eric S. Wiedner,^a Shannon S. Stahl,^b Aaron M. Appel^{a*}

^aCenter for Molecular Electrocatalysis, Pacific Northwest National Laboratory, Richland, WA 99352, USA. *E-mail: aaron.appel@pnnl.gov

^bDepartment of Chemistry, University of Wisconsin–Madison, Madison, Wisconsin 53706-1322, USA.

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1. Tabulated values of $\Delta G^{\circ}_{+n \text{ H2 } (g)}$

The values of $\Delta G_{f^{\circ}}$ in Table S1 were taken from the CRC Handbook of Chemistry and Physics¹ or the NIST Chemistry WebBook² (either directly or via calculation from $\Delta H_{f^{\circ}}$ and S°). To our knowledge, gasphase ΔG_{f}° are not available for benzyl alcohol and benzoic acid. The values were therefore calculated from liquid-phase (BnOH) or solid-state (PhCO₂H) ΔG_{f}° and the vapor pressure at 298 K taken from the PubChem database³ ($\Delta G_{(s \text{ or } 1 \rightarrow g)}^{\circ} = -RT \ln(P)$).

Table S1. Values of ΔG°_{f} used for calculation of ΔG°_{+n}	i2 (g)
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	∆ <i>G</i> f [°] (g) (kJ/mol)
H ₂ O	-228.6
MeOH	-162.3
EtOH	-167.9
ⁱ PrOH	-173.2
BnOH	-4.6
HCHO	-102.5
MeCHO	-133.0
Me ₂ CO	-152.6
HC(O)OMe	-299.9
EtOAc	-329.5
HCO ₂ H	-351.0
AcOH	-375.1
PhCO₂H	-210.7
CO ₂	-394.4

The values of $\Delta G^{\circ}_{+n H2 (g)}$ in Table S2 were calculated as follows:

Alcohol \rightarrow Aldehyde or ketone:	$\Delta G^{\circ}_{+H2 (g)} = \Delta G^{\circ}_{f}(alcohol_{(g)}) - \Delta G^{\circ}_{f}(aldehyde/ketone_{(g)})$
Alcohol \rightarrow Ester:	$\Delta G^{\circ}_{+2 \text{ H2 }(g)} = 2^{*} \Delta G^{\circ}_{f} (\text{alcohol}_{(g)}) - \Delta G^{\circ}_{f} (\text{ester}_{(g)})$
Alcohol \rightarrow Carboxylic acid:	$\Delta G^{\circ}_{+2 \text{ H2 (g)}} = \Delta G^{\circ}_{f} (\text{alcohol}_{(g)}) + \Delta G^{\circ}_{f} (H_2O_{(g)}) - \Delta G^{\circ}_{f} (\text{carboxylic acid}_{(g)})$
Methanol \rightarrow CO ₂ :	$\Delta G^{\circ}_{+3 \text{ H2 }(g)} = \Delta G^{\circ}_{\text{f}} \left(\text{MeOH}_{(g)} \right) + \Delta G^{\circ}_{\text{f}} \left(\text{H}_2 \text{O}_{(g)} \right) - \Delta G^{\circ}_{\text{f}} \left(\text{CO}_{2(g)} \right)$

Table S2. Values of $\Delta G^{\circ}_{+n \text{ H2 (g)}}$ (n = 1, 2, 3)

Alcohol	∆ <i>G</i> ° _{+H2 (g)} (kcal/mol)	Ester ∆G° _{+2 H2 (g)} (kcal/mol)	Carboxylic Acid ∆G° _{+2 H2 (g)} (kcal/mol)	∆ <i>G</i> ° _{+3 H2 (g)} (kcal/mol)
MeOH	-14.3	-5.9	-9.5	0.8
EtOH	-8.3	-1.5	-5.1	
iPrOH	-4.9			
BnOH	-6.0ª		-5.4	

^a $\Delta G^{\circ}_{+H2 (g)}$ for dehydrogenation of BnOH to give PhCHO was taken directly from a literature source.⁴

2. Calculation of equilibrium potentials from EBH+/H2 (org)

2a. Calculation from E°H+/H2 (org) and pKa

 $E^{\circ}{}'_{\text{product/R2CHOH (org)}}$ can be calculated from $E^{\circ}_{\text{H+/H2 (org)}}$ and p K_{a} (HBase⁺) as shown in Figure 3 in the main text for 2-electron oxidation of alcohols to aldehydes or ketones. Values of $E^{\circ}_{\text{H+/H2 (org)}}$ are presented in Table S3.

Solvent	<i>Е</i> ° _{H+/H2} (V vs Fc ^{+/0})	Ref.
MeCN	-0.028	5
THF	-0.343 (see note)	6
DME	-0.662ª	7
Divit	-0.62 ^b	8
DMSO	-0.67 ^b	8
DMA	-0.79	9
2-propanol	-0.494	10

Table S3. Values of E°H+/H2 (org)

^a Determined via OCP measurements with [H(DMF)][OTf] ^bDetermined from the cyclic voltammogram of HClO₄ with corrections by Fourmond et. al.

Note on $E^{\circ}_{H+/H2}$ and p K_a scale in THF:

When using $E^{\circ}_{H+/H2}$ to determine $E_{BH+/H2}$, it is critical to ensure that the appropriate pK_a scale is used. For THF, the most widely used pK_a scale was developed by Leito and co-workers. In their original studies^{11, 12}, relative ion pair acidities (ΔpK_{ip}) in THF were used to determine approximate relative pK_a values. The pK_a scale was then anchored with $pK_a(HNEt_3^+) = 12.5$ based on previous work¹³ by Morris and co-workers. These values were originally referred to as pK_a values to indicate that they are estimates and not directly measured pK_a values. In subsequent work, absolute pK_a values were measured for a set of 11 acids using potentiometric measurements.¹⁴ This study determined a pK_a of 13.7 for HNEt₃⁺, indicating that the anchor value for the pK_{α} scale is inaccurate. However, to avoid confusion regarding the anchor value, subsequent work continued to use the original inaccurate anchor value $pK_{\alpha}(HNEt_3^+) = 12.5$.¹⁵ We note that Leito and co-workers often do not make a distinction between pK_{α} values (*i.e.* values determined from ΔpK_{ip} using the inaccurate anchor value) as pK_a values (*i.e.* directly measured absolute values).¹⁶

The value of $E^{\circ}_{H+/H2}$ (THF) in Table S3 was calculated based on OCP measurements of $E_{BH+/H2}$ (THF) that were converted to $E^{\circ}_{H+/H2}$ (THF) using the absolute p K_a scale in ref 14. As discussed above, this p K_a scale is different from the much more commonly used p K_{α} scale. Only 11 absolute p K_a values have been directly measured in THF. However, p K_a values can be estimated from p K_{α} values¹⁴, which are available for a larger number of acids¹⁶:

 $pK_{a (THF)} = 1.02*pK_{a (THF)} + 2.14$

Therefore, when pK_{α} values are used in place of absolute pK_{α} values, $E_{BH+/H2 (THF)}$ is given by:

 $E_{\text{BH+/H2 (THF)}} = -0.343 - 0.0592^{*} (1.02^{*} p K_{\alpha \text{ (THF)}} + 2.14) = -0.470 - 0.0604^{*} p K_{\alpha \text{ (THF)}}$

Alternatively, the uncertainty associated with the p K_a scale in THF can be avoided by performing OCP measurements⁵ to directly determine $E_{BH+/H2 (THF)}$ with the acid-base pair being used in the catalytic reaction (see Section 2b). We note that this approach does not rigorously account for ion pairing effects,

which can have a particularly large impact on reaction energetics in solvents like THF that have low dielectric constants.¹³ This increases the uncertainty in $E_{BH+/H2}$ (and therefore in overpotentials) in THF relative to other solvents, although the impact is expected to be partially mitigated through buffering.

2b. Calculation from E_{BH+/H2 (org)}

In solvents where $E^{\circ}_{H+/H2 (org)}$ is not known or there is not an established p K_a scale, $E^{\circ'}$ for oxidation of alcohols can still be calculated by directly determining $E_{BH+/H2 (org)}$ from OCP measurements with the acid/base pair used in the catalytic reaction. This value is then combined with $\Delta G^{\circ}_{+n H2 (g)}$ and $\Delta \Delta G^{\circ}_{solv}$ to give $E^{\circ'}_{product/alcohol}$. As an example, a thermochemical scheme for calculation of $E^{\circ'}$ for 2-electron oxidation of alcohols is shown in Scheme S1.

Scheme S1. Calculation of $E^{\circ'}$ for 2-electron oxidation of alcohols to the corresponding aldehyde or ketone from an experimentally measured value of $E_{\text{BH+/H2 (org)}}$ and $\Delta G^{\circ}_{+\text{H2 (g)}}$

$$2 \text{ HBase}^{+}_{(\text{org})} + 2 \text{ e}^{-}_{(\text{Fc}^{+/0})} \longrightarrow \text{H}_{2(g)} + 2 \text{ Base}_{(\text{org})} \qquad \Delta G^{\circ} = -2FE_{\text{BH}^{+}/\text{H}_{2}}(\text{org})$$

$$R_{2}C=O_{(g)} + H_{2(g)} \longrightarrow R_{2}C(\text{H})-OH_{(g)} \qquad \Delta G^{\circ} + H_{2(g)}$$

$$R_{2}C=O_{(\text{org})} \longrightarrow R_{2}C=O_{(g)} \qquad -\Delta G^{\circ}_{\text{solv}}(R_{2}C=O)$$

$$R_{2}C(\text{H})-OH_{(g)} \longrightarrow R_{2}C(\text{H})-OH_{(\text{org})} \qquad \Delta G^{\circ}_{\text{solv}}(R_{2}C=O)$$

$$AG^{\circ}_{\text{solv}}(R_{2}C=O)$$

$$AG^{\circ}_{\text{solv}}(R_{2}C=O)$$

$$AG^{\circ}_{\text{solv}}(R_{2}C=O)$$

$$AG^{\circ}_{\text{solv}}(R_{2}C=O)$$

$$C^{\circ}_{\text{solv}}(R_{2}C=O)$$

$$C^{\circ}_{\text{solv}}(R_{$$

3. Estimation of $\Delta G^{\circ}_{solv (org)}$

Many of the thermochemical schemes in this work require solvation free energies in organic solvent. Very few of these values are directly available in the literature. In order to estimate some of them, we used a method that has been described previously⁷ involving vapor pressures over binary mixtures of solvents.

The free energy for transfer of a substrate A from the gas phase to solution can be calculated by

$$\mathsf{A}_{\mathsf{g}} \rightleftharpoons \mathsf{A}_{\mathsf{solv}} \quad \Delta G^{\circ}_{\mathsf{solv}} = RT \ln \left(\frac{P_{\mathsf{A}}}{[\mathsf{A}]_{(\mathsf{solv})}} \right)$$

where P_A is the vapor pressure of A over the solution (in atm) and $[A]_{(solv)}$ is the concentration of A in the solution (1 M for our chosen standard state). The solvation free energy of A can therefore be calculated from the vapor pressure of A over a 1 M solution of A.

In vapor-liquid equilibrium studies, the results are generally reported on a mole fraction basis. Assuming ideal mixing of the solute and solvent in the liquid phase (*i.e.* the volumes are additive), the mole fraction of a solute A in solution is converted to concentration by:

$$[A] = \frac{c_A}{\frac{c_A MW_A}{1000 d_A} + \frac{(1-c_A)MW_B}{1000 d_B}}$$

where χ , MW, and d are the solution-phase mole fraction, molecular weight, and density (in g/mL) of the solute (A) and solvent (B). Although vapor pressures are typically not reported at our chosen standard state of 1 M in solution, the vapor pressure of A over a 1 M solution of A can be estimated by assuming that the vapor pressure of A varies linearly with χ_A over a limited concentration range.

To demonstrate the validity of this approach, the solvation free energy of methanol in water was calculated from the vapor pressure of methanol over water (Figure S1).¹⁷ The resulting value ($\Delta G^{\circ}_{solv} = -2.7$ kcal/mol) is reasonably close to the reported solvation free energy of methanol in water ($\Delta G^{\circ}_{solv} = -3.2$ kcal/mol; see Table S5). The fits used to determine ΔG°_{solv} for MeOH and H₂O in THF and MeCN are shown in Figures S2-S6, and the resulting values are summarized in Table S4.

Table S4. Solvation free energies for methanol, water, and acetic acid in organic solution determined from vapor pressures

Solvent	∆ <i>G</i> ° _{solv} (MeOH) kcal/mol	∆ <i>G</i> ° _{solv} (H₂O) kcal/mol	∆ <i>G</i> ° _{solv} (AcOH) kcal/mol
MeCN	-2.0	-2.4	-4.0
THF	-2.5	-2.3	



Figure S1. Determination of vapor pressure of methanol over a 1 M solution of methanol in water (orange point) from known vapor pressures at other concentrations (shown in blue).¹⁷



Figure S2. Determination of vapor pressure of methanol over a 1 M solution of methanol in acetonitrile (orange point) from known vapor pressures at other concentrations (shown in blue).¹⁸



Figure S3. Determination of vapor pressure of methanol over a 1 M solution of methanol in THF (orange point) from known vapor pressures at other concentrations (shown in blue).¹⁹ These data were reported at 303 K rather than 298 K, but this is expected to have a very small impact (*ca.* 0.2 kcal/mol) on the final solvation free energy.



Figure S4. Determination of vapor pressure of water over a 1 M solution of water in acetonitrile from vapor pressures reported at 293 K (blue points) and 303 K (orange points). The extrapolated vapor pressures are shown in grey and yellow, respectively, at these two temperatures. The average of these values was used to estimate P_{H2O} at 298 K.²⁰



Figure S5. Determination of vapor pressure of water over a 1 M solution of water in THF (orange point) from known vapor pressures at other concentrations (shown in blue).²¹



Figure S6. Determination of vapor pressure of acetic acid over a 1 M solution of acetic acid in acetonitrile (orange point) from known vapor pressures at other concentrations (shown in blue).²²

4. Evaluation of standard potentials for 2-electron oxidation of alcohols

4a. Calculation of aqueous standard potentials for 2-electron oxidation of alcohols

We calculated aqueous standard potentials for oxidation of alcohols following the method described in the main text for calculation of $E^{\circ}_{R2CO/R2CHOH (org)}$ as shown in Scheme S2. This method requires $E^{\circ}_{H+/H2 (SHE)}$ (defined as zero), the values of $\Delta G^{\circ}_{+H2 (g)}$ (Table S2) and ΔG°_{solv} for the alcohol and aldehyde or ketone in water (Table S5). Values of ΔG°_{solv} were taken^a from the MNSOL database²³ or calculated^b from aqueous Ostwald solubility coefficients.²⁴ The resulting $E^{\circ}_{R2CO/R2CHOH (aq)}$ are compared to values reported in the literature in Table S6. A similar method has been used previously to estimate $E^{\circ}_{PhCHO/BnOH (aq)}$.²⁵

Scheme S2. Calculation of standard potentials for 2-electron alcohol oxidation in aqueous solution

$R_2C=O_{(aq)} + 2 H^+_{(aq)} + 2 e^{(SHE)} \longrightarrow R_2C(H)-OH_{(aq)}$	$\boldsymbol{E}^{\circ}_{R_{2}CO/R_{2}CHOH(aq)} = \boldsymbol{E}^{\circ}_{H^{*}/H_{2}(SHE)} + \frac{\Delta \boldsymbol{G}^{\circ}_{+H_{2}(g)} + \Delta \Delta \boldsymbol{G}^{\circ}_{solv}}{-2\boldsymbol{F}}$
$R_2C(H)-OH_{(g)} \longrightarrow R_2C(H)-OH_{(aq)}$	
$R_2C=O_{(aq)} \longrightarrow R_2C=O_{(g)}$	$\begin{bmatrix} AAG^{\circ} & - AG^{\circ} & (BACHOH) - AG^{\circ} & (BAC=O) \end{bmatrix}$
$R_2C=O_{(g)} + H_{2(g)} R_2C(H)-OH_{(g)}$	$\Delta G^{\circ} + H_{2(g)} = \Delta G^{\circ}_{f} \left(R_{2}CHOH_{(g)} \right) - \Delta G^{\circ}_{f} \left(R_{2}C=O_{(g)} \right)$
$2 H^+_{(aq)} + 2 e^{(SHE)} \longrightarrow H_{2(g)}$	$\Delta G^{\circ} = -2FE^{\circ}_{H^{+}/H_{2}}(SHE)$

Table S5. Aqueous solvation free energies used for calculation of $E^{\circ}_{R2CO/R2CHOH (aq)}$

	Alcohol ∆ <i>G</i> ° _{solv} (kcal/mol)	Aldehyde/ketone ∆G° _{solv} (kcal/mol)	∆∆G° _{solv} (kcal/mol)
MeOH/CH ₂ O	-3.2	-0.9	-2.3
EtOH/CH ₃ CHO	-3.1	-1.6	-1.5
ⁱ PrOH/Me ₂ CO	-2.9	-1.9	-0.9
BnOH/PhCHO	-4.5	-2.1	-2.3

^a The values in the MNSOL database are reported for a standard state of 1 M gas dissolving at a solution concentration of 1 M, which is often referred to as the Ben-Naim standard state and denoted as ΔG^* . To convert to the more conventional standard state of 1 atm gas and 1 M solution (ΔG°), a correction factor of $\Delta G^{*\to\circ} = RT \ln (V^\circ)$ must be added (where $V^\circ = RT$ is the volume occupied by an ideal gas at a pressure of 1 atm). At 298 K, $V^\circ = 24.45$ L and $\Delta G^{*\to\circ} = 1.89$ kcal/mol.

^b The Oswald solubility coefficient (*L*, commonly reported as log(L)) is a unitless quantity that represents the ratio of the concentrations of a gas in the liquid and gaseous phases. The solvation free energy can therefore be calculated as: $\Delta G^{\circ}_{solv} = -2.303 RT log(L) + \Delta G^{* \rightarrow \circ}$

where $\Delta G^{*\to\circ} = 1.89$ kcal/mol is added to convert from a 1 M gaseous standard state (implied by the use of Ostwald solubility coefficients) to a 1 atm standard state, as described above.

Table S6. Comparison of standard potentials for 2-electron alcohol oxidation reported in the literature to those calculated using the approach in Scheme S2.

	Calculated E°	Literature E°	Ref.
	(V vs SHE)	(V vs SHE)	
MeOH	0.361	0.232	26
EtOH	0.212	0.218	27
ⁱ PrOH	0.127	0.133	27

For the EtOH/acetaldehyde and ⁱPrOH/acetone pairs, the values of $E^{\circ}_{R2CO/R2CHOH (aq)}$ calculated in this fashion are within 10 mV of values reported in the literature. In contrast, the calculated value of $E^{\circ}_{R2CO/R2CHOH (aq)}$ for the methanol/formaldehyde pair is 130 mV more positive than the literature value. This is presumably due to a difference in the treatment of formaldehyde hydration. To our knowledge, neither early sources for values of $E^{\circ}_{H2CO/MeOH (aq)}$ nor sources for ΔG°_{solv} for formaldehyde explicitly discuss any corrections that were applied to account for formaldehyde hydration. The K_{eq} for formaldehyde hydration²⁸ is approximately 10³ corresponding to ~4 kcal/mol of additional driving force which has a substantial impact (*ca.* –90 mV) on the calculated value of $E^{\circ}_{H2CO/MeOH (aq)}$. However, it is difficult to determine the precise correction needed due to the complexity of the equilibria of aqueous formaldehyde in the presence of methanol.²⁹⁻³¹ The K_{eq} values for acetaldehyde and acetone hydration are smaller (2 and 0.001, respectively²⁸) and should have a negligible influence on $E^{\circ}_{R2CO/R2CHOH (aq)}$.

Similar considerations also apply for the 2-electron oxidation of methanol in organic solution. To our knowledge, the speciation of formaldehyde in organic solutions containing methanol has not been quantitatively studied, but as is the case in water, a complex mixture of oligomeric species is expected. Because of the difficulties associated with accurately describing the solution speciation of formaldehyde, when evaluating overpotentials for 2-electron oxidation of methanol in organic solvents we recommend comparing to $E^{\circ}_{CH2O/MeOH (org)}$. The resulting value corresponds to a lower limit on the overpotential.

4b. Evaluation of $\Delta \Delta G^{\circ}_{solv} \approx 0$ approximation for 2-electron oxidation of alcohols

The solvation free energies for the alcohol and aldehyde/ketone pairs discussed here can be calculated^a in both water and hexadecane (Table S7).²⁴ In water, $\Delta\Delta G^{\circ}_{solv}$ is at most –2.3 kcal/mol, corresponding to a 50 mV change in $E^{\circ}_{R2CO/R2CHOH (org)}$. In contrast, in the nonpolar, aprotic solvent hexadecane $\Delta\Delta G^{\circ}_{solv}$ is less than –1 kcal/mol corresponding to a shift in $E^{\circ}_{R2CO/R2CHOH (org)}$ of 15 mV or less. The magnitude of $\Delta\Delta G^{\circ}_{solv}$ in the polar, aprotic solvents typically used in electrochemical alcohol oxidation studies likely lies somewhere between these two extremes.

	In water			In hexadecane		
	Alcohol	Aldehyde/ketone	$\Delta\!\Delta G^{\circ}_{solv}$	Alcohol	Aldehyde/ketone	$\Delta \Delta G^{\circ}_{solv}$
	ΔG°_{solv}	ΔG°_{solv}	(kcal/mol)	ΔG°_{solv}	ΔG°_{solv}	(kcal/mol)
	(kcal/mol)	(kcal/mol)		(kcal/mol)	(kcal/mol)	
MeOH/CH ₂ O	-3.2	-0.9	-2.3	+0.6	+0.9	-0.3
EtOH/CH ₃ CHO	-3.1	-1.6	-1.5	-0.1	+0.2	-0.4
ⁱ PrOH/Me ₂ CO	-2.9	-1.9	-0.9	-0.6	-0.5	-0.1
BnOH/PhCHO	-4.5	-2.1	-2.3	-4.2	-3.5	-0.6

Table S7. Solvation free energies for alcohol-aldehyde/ketone pairs in water and hexadecane.

Further validation of the approximation $\Delta\Delta G^{\circ}_{solv} \approx 0$ in organic solvents is provided by comparisons between sets of ΔG°_{solv} in water, MeCN, and THF. For ethanol, values of ΔG°_{solv} have been reported^b in all 3 solvents.²³ Although ΔG°_{solv} for acetaldehyde are not reported in MeCN and THF, they have been reported^b for 2-butanone in all 3 solvents.²³ The aqueous ΔG°_{solv} for 2-butanone is similar to that of acetaldehyde. Assuming that the same is true in MeCN and THF, comparison of the ΔG°_{solv} of ethanol and 2-butanone gives a rough estimate of the magnitude of $\Delta\Delta G^{\circ}_{solv}$ for the ethanol/acetaldehyde pair in MeCN and THF. As shown in Table S8, this suggests $\Delta\Delta G_{solv} \approx 0$ in both solvents.

Table S8. Solvation free energies for 2-butanone and ethanol in water, MeCN, and THF.

Solvent	∆ <i>G</i> ° _{solv} (kcal/mol) Ethanol	∆ <i>G</i> ° _{solv} (kcal/mol) Acetaldehyde	∆ <i>G</i> ° _{solv} (kcal/mol) 2-butanone
H₂O	-3.1	-1.6	-1.8
MeCN	-2.5	-	-2.8
THF	-2.7	-	-2.7

^a See Section 4a for the method used to calculate ΔG°_{solv} from Ostwald solubility coefficients

^b A standard state correction (see Section 4a) was applied to the values taken from the MNSOL database.

4c. Alternative thermochemical schemes for calculation of E°R2CO/R2CHOH (org)

Here, we present two alternative schemes for calculation of $E^{\circ}_{R2CO/R2CHOH (org)}$. As detailed below, we believe the values calculated from $\Delta G^{\circ}_{+H2 (g)}$ as described in the main text of this paper are more accurate than those determined using these two schemes.

4c.i. Calculation from E°R2CO/R2CHOH (aq)

In previous reports, thermochemical cycles have been used to convert aqueous standard potentials to standard potentials in organic solution using $E^{\circ}_{H+/H2}$ in water and organic solution along with free energies for transfer of the substrate and product from water to organic solution.^{7, 32} A scheme for converting $E^{\circ}_{R2CO/R2CHOH (aq)}$ to $E^{\circ}_{R2CO/R2CHOH (org)}$ using this method is shown below.

Scheme S3. Thermochemical scheme for calculation of standard potentials for alcohol oxidation to ketones/aldehydes in organic solution starting from aqueous standard potentials.



The free energy for transferring the aldehyde/ketone and alcohol from water to organic solution $(\Delta G^{\circ}_{tr, aq \rightarrow org})$ is not known in most cases and is challenging to measure experimentally. Calculation of $\Delta \Delta G^{\circ}_{tr, aq \rightarrow org}$ is particularly difficult for the formaldehyde/methanol couple because of the complex solution behavior of formaldehyde, as discussed in Section 4a.

The quantity $\Delta\Delta G^{\circ}_{tr, aq \rightarrow org}$ can also be expressed in terms of a difference in solvation free energy differences between the alcohol and aldehyde/ketone in organic solution and water:

 $\Delta\Delta G^{\circ}_{\text{tr, aq} \rightarrow \text{org}} = \Delta\Delta G^{\circ}_{\text{solv, org}} - \Delta\Delta G^{\circ}_{\text{solv, aq}}$

As discussed in Section 4b, it is unlikely that $\Delta\Delta G^{\circ}_{solv, org}$ and $\Delta\Delta G^{\circ}_{solv, aq}$ are identical. We therefore recommend estimating $E^{\circ}_{R2CO/R2CHOH (org)}$ from $\Delta G_{+H2 (g)}$ rather than from $E^{\circ}_{R2CO/R2CHOH (aq)}$, although the resulting values will be similar since the magnitude of $\Delta\Delta G^{\circ}_{solv}$ is small in water (see Table S7) and is expected to be small in organic solvents as well.

4.c.ii Calculation from hydricity of isopropoxide

An alternative thermochemical cycle for determination of the acetone/2-propanol standard potential in acetonitrile has been proposed previously.³³ This cycle uses a computationally derived value for the hydricity of isopropoxide and an estimated p*K*_a of 38 for 2-propanol in acetonitrile. Neither of these values is known to a high degree of accuracy, and since hydricities for other alkoxides have not been calculated the method is not easily extended to other alcohol-aldehyde/ketone pairs. The value of $E^{\circ}_{Me2CO/iPrOH (MeCN)}$ calculated using this cycle is 250 mV more negative than the value determined from $\Delta G^{\circ}_{+H2 (g)}$.



Scheme S4. Calculation of standard potential for 2-propanol oxidation using hydricity of isopropoxide

5. Evaluation of E° for 4-electron oxidation of alcohols to esters

5a. Calculation of standard potentials for 4-electron oxidation of alcohols to esters

Following the approach outlined in the main text for 2-electron oxidation of alcohols to aldehydes or ketones, the standard potential for 4-electron oxidation of alcohols to esters can be calculated using the thermochemical cycle in Scheme S5. The $\Delta\Delta G^{\circ}_{solv}$ term can be omitted when experimental values are not known since it is likely that $\Delta\Delta G^{\circ}_{solv}$ makes a relatively small contribution to $E^{\circ}_{ester/alcohol}$ (see Section 5b).

Scheme S5. Thermochemical scheme for calculation of standard potential for 4-electron oxidation of alcohols to esters.



5b. Calculation of E^oEtOAc/EtOH (MeCN)

A thermochemical scheme for determination of the standard potential for ethanol oxidation to ethyl acetate in MeCN is shown in Scheme S6. $\Delta G^{\circ}_{solv, EtOH (MeCN)}$ was taken^a from the literature.²³ $\Delta G^{\circ}_{solv, EtOAc (MeCN)}$ was calculated from the aqueous solvation free energy^a for EtOAc²³ and the free energy for transfer of EtOAc from water to MeCN (Scheme S7).³⁴ The solvation energy terms make only a small contribution (17 mV) to $E^{\circ}_{EtOAc/EtOH (MeCN)}$.

Scheme S6. Thermochemical scheme for determination of standard potential for ethanol oxidation to ethyl acetate in acetonitrile.

$4 H^{+}_{(MeCN)} + 4 e^{-}_{(Fc^{+/0})}$	2 H _{2(g)}	$\Delta G^{\circ} = -4FE^{\circ}_{H^{+}/H_{2}(Fc^{+/0})} = +2.6 \text{ kcal/mol}$
EtOAc _(g) + 2 H _{2(g)}	2 EtOH _(g)	$\Delta G^{\circ}_{+2 H_2(g)}$ = –1.5 kcal/mol
EtOAc _(MeCN)	EtOAc _(g)	$-\Delta G^{\circ}_{\text{solv, EtOAc (MeCN)}}$ = +3.4 kcal/mol
2 EtOH _(g)	2 EtOH _(MeCN)	$2^{*}\Delta G^{\circ}_{solv, EtOH (MeCN)} = 2^{*}-2.5 \text{ kcal/mol}$
$EtOAc_{(MeCN)} + 4 H^{+}_{(MeCN)} + 4 e^{-}_{H^{+}/H_{2}(Fc^{+/0})}$	2 EtOH _(MeCN)	$\boxed{E^{\circ}_{EtOAc/EtOH (MeCN)} = + 0.01 \text{ V vs Fc}^{+/0}}$
Scheme S7. Calculation of ΔG°_{solv} for EtOAc in MeC	N	
EtOAc _(g) EtOAc _(aq)	$\Delta G^{\circ}_{\text{solv (aq)}} = -1.2$	2 kcal/mol
EtOAc _(aq)	$\Delta {m G}^{m \circ}_{m tr,\; {\sf EtOAc}}$ (aq $ ightarrow$ or	_{rg)} = – 2.2 kcal/mol
EtOAc _(g)	$\Delta G^{\circ}_{solv (MeCN)} = -$	3.4 kcal/mol

^a A standard state correction (see Section 4a) was applied to the values taken from the MNSOL database

6. Evaluation of E° and $E^{\circ'}$ for 4-electron oxidation of alcohols to carboxylic acids and carboxylates

6a. Calculation of aqueous standard potentials for oxidation of alcohols to carboxylic acids

A thermochemical scheme for 4-electron oxidation of alcohols to carboxylic acids is shown in Scheme S8. Solvation free energies for carboxylic acids and alcohols were calculated^a from reported dimensionless Henry's law coefficients or Ostwald coefficients.^{24, 35} For a reference state of liquid water^b, the solvation free energy of water in water (*i.e.* the free energy for vaporization of water) is given by:

 $\Delta G^{\circ}_{solv, H2O} = RT \ln(P_{vapor}) = RT \ln (0.0313 atm) = -2.1 kcal/mol$

The vapor pressure of water at 298 K was taken from the literature.¹ The resulting potentials for oxidation of methanol, ethanol, and benzyl alcohol are provided in Table S9.

Below the p K_a of the carboxylic acid, the thermodynamic potential shifts by $-2.303^*RT/F = -59 \text{ mV}$ per pH unit according to the Nernst equation. Above the p K_a of the carboxylic acid, the potential shifts by $-5^*2.303^*RT/(4F) = -74 \text{ mV}$ per pH unit (reflecting the 4 e⁻/ 5 H⁺ stoichiometry of the reaction), resulting in the following expression for $E^{\circ}_{RCO2^*/RCH2OH}$:

 $E^{\circ}_{RCO2-/RCH2OH} = E^{\circ}_{RCO2H} - 0.059^{*}pK_{a}(RCO_{2}H) - 0.074^{*}(pH-pK_{a}(RCO_{2}H))$ = $E^{\circ}_{RCO2H} + 0.015^{*}pK_{a}(RCO_{2}H) - 0.074^{*}pH$

Scheme S8. Calculation of standard potential for oxidation of alcohols to carboxylic acids.

$RCO_2H_{(aq)} + 4 H_{(aq)}^* + 4 e_{(SHE)}^-$	RCH ₂ OH _(aq) + H ₂ O _(aq)	E° _{RCO2H/RCH2OH (aq)} =	$E^{\circ}_{H+/H2 (aq)} + \frac{\Delta G^{\circ}_{+2 H_2 (g)} + \Delta \Delta G^{\circ}_{solv}}{-4F}$	
H ₂ O _(g)	H ₂ O _(aq)	$\Delta {\sf G}^{\circ}{}_{\sf solv,\; \sf H2O\;(\sf aq)}$ _		
RCH ₂ OH _(g)	$RCH_2OH_{(aq)} \qquad \Delta G^\circ_{solv, RCH2OH(aq)} \qquad \Delta \Delta G^\circ_{solv} = \Delta G^\circ_{solv}$		$\Delta \Delta G^{\circ}_{\text{solv}} = \Delta G^{\circ}_{\text{solv}} (\text{RCH}_2\text{OH}) + \Delta G^{\circ}_{\text{solv}}(\text{H}_2\text{O}) - \Delta G^{\circ}_{\text{solv}} (\text{RCO}_2\text{H})$	
RCO ₂ H _(aq)	$RCO_2H_{(g)}$	$-\Delta G^\circ_{ m solv, \ RCO2H}$ (aq)		
$RCO_2H_{(g)} + 2 H_{2(g)}$	$\text{RCH}_2\text{OH}_{(g)} + \text{H}_2\text{O}_{(g)}$	$\Delta G^{\circ}_{+2 \text{ H2}(g)} = \Delta G^{\circ}_{f} (\text{RCH}_2\text{OH}_{(g)}) + \Delta G^{\circ}_{f} (\text{H}_2\text{O}_{(g)}) - \Delta G^{\circ}_{f} (\text{RCO}_2\text{H}_{(g)})$		
4 H ⁺ _(aq) + 4 e ⁻ _(SHE)	2 H _{2(g)}	ΔG° = $-4FE^\circ_{H^+/H^2}$ (aq	₎ = 0 kcal/mol	

Table 03. Thermodynamic potentials for oxidation of alconois to carboxylic acids of carboxylat	Table S9. Thermore	dynamic potentials f	or oxidation of	f alcohols to ca	arboxylic acids or	carboxylates
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	∆ <i>G</i> ° _{solv, RCH2OH} (kcal/mol)	∆ <i>G</i> ° _{solv, RCO2H} (kcal/mol)	∆∆ <i>G</i> ° _{solv} (kcal/mol)	E⁰ _{RCO2H/RCH2OH} (V vs SHE)	p <i>K</i> ₄(RCO₂H)³	<i>Е</i> °′ _{RCO2–/RCH2OH} (V vs SHE)
MeOH	-3.2	-5.1	-0.2	0.11	3.75	0.16–0.074*pH
EtOH	-3.1	-5.1	-0.1	0.06	4.76	0.13–0.074*pH
BnOH	-4.5	-6.1	-0.5	0.06	4.20	0.13–0.074*pH

$$\Delta G^{\circ}_{\text{solv}} = -2.303 \ RT \log(K_{\text{AW}}) + \Delta G^{* \to \circ}$$

where $\Delta G^{*\to\circ} = 1.89$ kcal/mol is added to convert from a 1 M gaseous standard state to a 1 atm standard state.

^a The dimensionless Henry's law constant (K_{AW}) is equivalent to the Ostwald coefficient (see Section 4a). The solvation free energy is therefore calculated as:

^b In some literature sources (including values in the MNSOL database), self-solvation free energy (the solvation free energy of a liquid in itself) is instead calculated as $\Delta G^{\circ}_{solv} = RT \ln (P_{vapor} / M_{liq})$ where P_{vapor} is the vapor pressure of the liquid and M_{liq} is the molarity of the pure liquid. If this method is used for water, it implies a reference state of 1 M water in water, which differs from the reference state of 55 M water implied by our calculation of the solvation free energy as $\Delta G^{\circ}_{solv} = RT \ln (P_{vapor})$.

6b. Calculation of standard potentials for oxidation of alcohols to carboxylic acids in organic solution

A thermochemical cycle for 4-electron oxidation of alcohols to carboxylic acids in organic solution is shown in Scheme S9. Scheme S10 shows the cycle for oxidation of alcohols to carboxylate salts in the presence of strong bases where $pK_a(HBase^+) > pK_a(RCO_2H)$.

Scheme S9. Calculation of *E*° for 4-electron oxidation of primary alcohols to carboxylic acids.



 $\operatorname{RCO}_{2^{-}(\operatorname{org})}^{-} + 5 \operatorname{HBase}^{+}_{(\operatorname{org})} + 4 \operatorname{e}^{-}_{(\operatorname{Fc}^{+0})} \xrightarrow{} \operatorname{RCH}_{2}\operatorname{OH}_{(\operatorname{org})} + H_{2}\operatorname{O}_{(\operatorname{org})} + 5 \operatorname{Base}_{(\operatorname{org})} \xrightarrow{} E^{\circ'}_{\operatorname{RCO}_{2^{-}/\operatorname{RCH}_{2}}\operatorname{OH}(\operatorname{org})}$

 $E^{\circ}{}'_{\text{RCO}_{2}^{-7}/\text{RCH}_{2}\text{OH (org)}} = E^{\circ}_{\text{RCO}_{2}\text{H}/\text{RCH}_{2}\text{OH (org)}} + \frac{-1.364^{*}\text{p}K_{a}(\text{RCO}_{2}\text{H}) + 5^{*}1.364^{*}\text{p}K_{a}(\text{HBase}^{+})}{-1.364^{*}\text{p}K_{a}(\text{RCO}_{2}\text{H}) + 5^{*}1.364^{*}\text{p}K_{a}(\text{HBase}^{+})}$

-4F

 $E^{\circ}{}'_{\text{RCO}_2^{-}/\text{RCH}_2\text{OH (org)}} = E^{\circ}_{\text{RCO}_2\text{H/RCH}_2\text{OH (org)}} + 0.015^*\text{p}K_a(\text{RCO}_2\text{H}) - 0.074^*\text{p}K_a(\text{HBase}^+)$

6c. Calculation of E°_{ACOH/EtOH} (MeCN) and E°_{ACO-/EtOH} (MeCN)

A thermochemical scheme for calculation of $E^{\circ}_{ACOH/EtOH (MeCN)}$ is presented in Scheme S11. The values of $\Delta G^{\circ}_{solv, AcOH/MeCN}$ and $\Delta G^{\circ}_{solv, H2O/MeCN}$ were determined as described in Section 3, and $\Delta G^{\circ}_{solv, EtOH/MeCN}$ was taken^a from the literature.²³ For this system, $\Delta \Delta G^{\circ}_{solv} = -0.9$ kcal/mol, corresponding to a 10 mV contribution to the final potential.

Scheme S11. Calculation of the standard potential for oxidation of ethanol to acetic acid in acetonitrile.

$CH_3CO_2H_{(MeCN)} + 4 H^+_{(MeCN)} + 4 e^{(Fc^{+/0})}$	EtOH _(MeCN) + H ₂ O _(MeCN)	Е° _{АсОН/ЕtOH (MeCN)} = + 0.04 V vs Fc ^{+/0}
H ₂ O _(g)	H ₂ O _(MeCN)	$\Delta G^{\circ}_{solv, H2O (MeCN)}$ = -2.4 kcal/mol
EtOH _(g)	EtOH _(MeCN)	$\Delta G^{\circ}_{\text{solv, EtOH (MeCN)}}$ = -2.5 kcal/mol
CH ₃ CO ₂ H _(MeCN)	$CH_3CO_2H_{(g)}$	$-\Delta G^{\circ}_{\text{solv, AcOH (MeCN)}}$ = +4.0 kcal/mol
$CH_3CO_2H_{(g)} + 2H_{2(g)}$	$EtOH_{(g)} + H_2O_{(g)}$	$\Delta G^{\circ}_{+2 H2(g)}$ = -5.1 kcal/mol
$4 H^{+}_{(MeCN)} + 4 e^{-}_{(Fc^{*/0})}$	2 H _{2(g)}	$\Delta G^{\circ} = -4FE^{\circ}_{H+/H2 (MeCN)} = 2.6 \text{ kcal/mol}$

The p K_a of acetic acid in acetonitrile is 23.5.³⁶ The thermodynamic potential of the acetate/ethanol couple in acetonitrile is therefore:

 $E^{\circ}{}'_{ACO^{-}/EtOH} = 0.040 + 0.015^{*}23.5 - 0.074^{*}pK_{a}(HBase^{+}) = 0.393 - 0.074^{*}pK_{a}(HBase^{+}) V vs Fc^{+/0}$

^a A standard state correction (see Section 4a) was applied to the values taken from the MNSOL database

6d. Alternative thermochemical scheme for calculation of E°_{HCO2H/MeOH (MeCN)}

An alternative thermochemical scheme for calculation of $E^{\circ}_{\text{HCO2H/MeOH} (MeCN)}$ is presented in Scheme S12. In this approach, $E^{\circ}_{\text{CO2/HCO2H} (MeCN)}$ is calculated from the hydricity of formate in acetonitrile as described by Kubiak and co-workers.³⁷ The resulting value is combined with $E^{\circ}_{\text{CO2/MeOH} (MeCN)}$ calculated in Section 7b. The p K_{a} of formic acid³⁸, hydricity of formate³⁹, and $\Delta G^{\circ}_{\text{H+/H}^{-40}}$ in acetonitrile were taken from the literature. The resulting value of is nearly identical to the approximate value obtained from $\Delta G^{\circ}_{+2 \text{ H2 (g)}}$ (without a correction for $\Delta \Delta G^{\circ}_{\text{solv}}$).





7. Evaluation of E° for 6-electron oxidation of methanol to CO₂

7a. Calculation of E°CO2/MeOH (aq)

 $E^{\circ}_{\text{CO2/MeOH (aq)}}$ can be calculated from $\Delta G^{\circ}_{+3 \text{ H2 (g)}}$ and aqueous solvation free energies, as shown in Scheme S13. The resulting value of $E^{\circ}_{\text{CO2/MeOH (aq)}}$ agrees with literature reports which give $E^{\circ}_{\text{CO2/MeOH (aq)}} = +0.033 \text{ V vs SHE}.^{41, 42}$

Scheme S13. Calculation of $E^{\circ}_{CO2/MeOH (aq)}$ from $\Delta G^{\circ}_{+3 H2 (g)}$



The aqueous solvation free energy of methanol was taken from the literature (see Section 4a) and the solvation free energy of water in water was calculated as described in Section 6a.

7b. Calculation of E°CO2/MeOH (MeCN)

 $E^{\circ}_{CO2/MeOH (MeCN)}$ can be calculated from $\Delta G^{\circ}_{+3 H2 (g)}$ and the solvation free energies of methanol and water in MeCN (see Section 3). The final value of $E^{\circ}_{CO2/MeOH (MeCN)}$ is 0.00 V vs Fc^{+/0}, and the solvation free energy terms contribute –4.4 kcal/mol (+0.03 V) to the potential.





Using an analogous scheme, in THF the final value of $E^{\circ}_{CO2/MeOH (THF)}$ is -0.31 V vs Fc^{+/0}, and the solvation free energy terms contribute -4.8 kcal/mol (+0.03 V) to the potential.

7c. Calculation of E°CO2/MeOH (org) from E°CO2/MeOH (aq)

An alternative thermochemical cycle for calculating $E^{\circ}_{CO2/MeOH (org)}$ that starts from $E^{\circ}_{CO2/MeOH (aq)}$ is shown in Scheme S14. This cycle requires free energies for transfer of methanol and water from water to organic solvent ($\Delta G^{\circ}_{tr (aq \rightarrow org)}$).

Scheme S15. Calculation of E°CO2/MeOH (org) starting from E°CO2/MeOH (aq).



 $E^{\circ}_{\text{CO2/MeOH (org)}} = E^{\circ}_{\text{CO2/MeOH (aq)}} - E^{\circ}_{\text{H+/H2 (aq)}} + E^{\circ}_{\text{H+/H2 (org)}} + \frac{\Delta G^{\circ}_{\text{tr (aq \to org)}}}{-6F}$ $\boxed{E^{\circ}_{\text{CO2/MeOH (org)}} \approx 0.03 + E^{\circ}_{\text{H+/H2 (org)}}}$

Free energies for transfer of a substance A from water to organic solution can be calculated from the aqueous and organic solvation free energies of A as shown in Scheme S16.



Scheme S16. Calculation of $\Delta G^{\circ}_{tr (aq \rightarrow org)}$ from solvation free energies in water and organic solvent.

The free energies for transfer of methanol and water from water to organic solution (THF, MeCN) are presented in Table S10. The sources of the ΔG°_{solv} used in these calculations were presented in Section 3. The transfer free energies contribute less than 10 mV to $E^{\circ}_{CO2/MeOH (org)}$, demonstrating that it is reasonable to omit transfer free energies in estimations of $E^{\circ}_{CO2/MeOH (org)}$ from $E^{\circ}_{CO2/MeOH (aq)}$ in other solvents if estimates are not available.

Table S10. Transfer free energies relevant to methanol oxidation to CO2

	MeCN	THF
Δ G^otr (aq → org), MeOH (kcal/mol)	+1.2	+0.7
$\Delta \boldsymbol{G}^{o}_{tr} (aq \rightarrow org), H2O} (kcal/mol)$	-0.4	-0.2
Total ∆ <i>G</i> ° _{tr (aq→org)} (kcal/mol)	+0.8	+0.5
Contribution to E°CO2/MeOH (mV)	-6	-3

8. Calculation of standard potentials from liquid-phase ΔG°_{f}

While this work was in preparation, thermodynamic potentials were reported for several of the couples discussed here in acetonitrile.⁴³ The approach used to derive these values is similar to that described in this work, but starts from liquid-phase values of $\Delta G^{\circ}_{\rm f}$ in most cases and therefore involves a correction for the free energy of mixing the liquid with acetonitrile rather than the solvation free energy, as shown in Scheme S17 for 2-electron oxidation as an example. The values calculated using these two methods are within expected error of each other (Table S11), which provides further support for our assumption that solvation free energies do not make a substantial contribution to standard potentials.

Scheme S17. Calculation of $E^{\circ}_{R2CO/R2CHOH (MeCN)}$ from liquid-phase ΔG°_{f}

 $2 H^{+}_{(MeCN)} + 2 e^{-}_{(Fc^{+/0})} \longleftrightarrow H_{2(g)} \qquad \Delta G^{\circ} = -2FE^{\circ}_{H^{+}/H_{2}(org)}$ $R_{2}C=O_{(I)} + H_{2(g)} \bigoplus R_{2}C(H)-OH_{(I)} \qquad \Delta G^{\circ}_{+H_{2}(I)} = \Delta G^{\circ}_{f}(R_{2}CHOH_{(I)}) - \Delta G^{\circ}_{f}(R_{2}C=O_{(I)})$ $R_{2}C=O_{(MeCN)} \bigoplus R_{2}C=O_{(I)}$ $R_{2}C(H)-OH_{(I)} \bigoplus R_{2}C(H)-OH_{(MeCN)} \qquad \int \Delta G^{\circ}_{mix} = \Delta G^{\circ}_{mix}(R_{2}CHOH_{(MeCN)}) - \Delta G^{\circ}_{mix}(R_{2}C=O_{(MeCN)})$ $R_{2}C=O_{(MeCN)} + 2 H^{+}_{(MeCN)} + 2 e^{-}_{(Fc^{+/0})} \bigoplus R_{2}C(H)-OH_{(MeCN)} \qquad E^{\circ}_{R_{2}CO/R_{2}CHOH(MeCN)} = E^{\circ}_{H^{+}/H_{2}(MeCN)} + \frac{\Delta G^{\circ}_{+H_{2}(I)} + \Delta \Delta G^{\circ}_{mix}}{2E}$

Table S11. Comparison of standard potentials for oxidation of alcohols derived by Fokin et. al. to those calculated in this work.

	Fokin et. al. (V vs Fc ^{+/0})	This work (V vs Fc ^{+/0})
$MeCHO_{(g)} + 2 H^{+}_{(MeCN)} + 2 e^{-}_{(Fc+/0)} \rightarrow EtOH_{(MeCN)}$	0.207 ^a	0.15
Me ₂ CO _(MeCN) + 2 H ⁺ + 2 e [−] _(Fc+/0) → ⁱ PrOH _(MeCN)	0.089	0.08
EtOAc _(MeCN) + 4H ⁺ + 4 e [−] _(Fc+/0) → 2 EtOH _(MeCN)	0.025	0.01
$HCO_{2}H_{(MeCN)} + 4H^{+}_{(MeCN)} + 4e^{-}_{(Fc+/0)} \rightarrow MeOH_{(MeCN)} + H_{2}O_{(MeCN)}$	0.096	0.08
$AcOH_{(MeCN)} + 4H^{+}_{(MeCN)} + 4 e^{-}_{(Fc+/0)} \rightarrow EtOH_{(MeCN)} + H_2O_{(MeCN)}$	0.047	0.04
$CO_{2(g)} + 6H^{+}_{(MeCN)} + 6 e^{-}_{(Fc+/0)} \rightarrow MeOH_{(MeCN)} + H_2O_{(MeCN)}$	0.034	0.00

^a Fokin et. al. use a gas-phase standard state for acetaldehyde

9. Determination of overpotentials for BnOH and ⁱPrOH oxidation with [Ni(P^{tBu}₂N^{tBu}₂)(MeCN)₂][BF₄]₂ under buffered conditions

Experimental details

[Ni(PtBu₂NtBu₂)(MeCN)₂][BF₄]₂ was synthesized as described previously.⁴⁴ Acetonitrile was passed through neutral alumina on an Innovative Technology solvent purification system, distilled from calcium hydride, and stored over 3 Å molecular sieves. Tetrabutylammonium tetrafluoroborate was recrystallized from ethyl acetate. Benzyl alcohol (Acros, 98+% extra dry) was degassed and stored on 3 Å molecular sieves. Benzaldehyde was purified by vacuum distillation. Acetone (Acros, 98+% extra dry) was degassed and used without further purification. 2-propanol and triethylamine were distilled from calcium hydride and stored over molecular sieves. Triethylammonium tetrafluoroborate was prepared following a literature procedure.⁴⁵

Cyclic voltammetry measurements were performed using a CH Instruments 620D instrument. Experiments were performed in a glovebox at 22 – 24 °C using a standard 3-electrode setup consisting of a 1 mm PEEK-encased glassy carbon working electrode, a glassy carbon rod counter electrode, and a silver wire pseudoreference electrode separated from the analyte solution by a Vycor frit. The working electrode was polished with 0.25 μ m diamond paste (Buehler) between measurements.

The catalytic turnover frequency (k_{obs}) was calculated from cyclic voltammograms in the absence and presence of substrate:

$$\frac{i_{\text{cat}}}{i_{\text{p}}} = \frac{n}{0.4463} \sqrt{\frac{RTk_{\text{obs}}}{F\nu}}$$

where i_{cat} is the peak catalytic current (selected as the point at which a plot of the first derivative of current vs potential reaches a constant value), i_p is the peak current of the catalyst in the absence of substrate, n = 2 is the number of electrons required for catalytic turnover, R is the universal gas constant, T is the temperature, F is Faraday's constant, and v is the scan rate.

Oxidation of benzyl alcohol

For a 1:1 solution of benzyl alcohol to benzaldehyde and triethylamine to triethylammonium, the equilibrium potential for benzyl alcohol oxidation is given by:

$$E^{\circ}{}^{\prime}_{PhCHO/BnOH (org)} = E^{\circ}{}_{H^{+}/H_{2} (Fc^{+/0})} - 0.0592^{*}pK_{a}(Et_{3}NH^{+}) + \frac{\Delta G^{+}{}_{H_{2} (g)}}{-2F}$$
$$E^{\circ}{}^{\prime}_{PhCHO/BnOH (org)} = -0.028 - 0.0592^{*}18.8 + \frac{-6.0}{-2\times23.06} = -1.01 \text{ V vs Fc}^{+/0}$$

We chose not to conduct electrochemical studies with $[Ni(Pt^{Bu}_2N^{Bu}_2)(MeCN)_2]^{2+}$ under these conditions for two reasons. First, a significant increase in *i*_{cat} was observed in the presence of equimolar benzaldehyde and benzyl alcohol. The reason for the current increase is not known, but could be due to formation of an ester, as observed in chemical oxidations with the related Ni complex $[Ni(Pt^{Bu}_2N^{Bn}_2)(MeCN)_2]^{2+}$.⁴⁶ Second, a significant decrease in *i*_{cat} was observed in the presence of equimolar triethylamine and triethylammonium, likely due to instability of the Ni complex in the presence of a large excess of acid, which was observed previously for $[Ni(Pt^{Bu}_2N^{Bn}_2)(MeCN)_2]^{2+}$.⁴⁷

Oxidation of benzyl alcohol under buffered conditions was therefore instead performed on a solution containing 200 mM benzyl alcohol, 20 mM benzaldehyde, 100 mM triethylamine, and 10 mM triethylammonium tetrafluoroborate. The equilibrium potential for benzyl alcohol oxidation under these conditions is calculated as follows:

$$E^{\circ'}{}_{PhCHO/BnOH (org)} = E^{\circ}{}_{H^{+}/H_{2} (Fc^{+/0})} - 0.0592^{*}pK_{a}(Et_{3}NH^{+}) + \frac{\Delta G^{\circ}{}_{+H_{2} (g)}}{-2F} - \frac{RT}{2F} ln\left(\frac{[BnOH][Et_{3}N]^{2}}{[PhCHO][Et_{3}NH^{+}]^{2}}\right)$$
$$E^{\circ'}{}_{PhCHO/BnOH (org)} = -0.028 - 0.0592^{*}18.8 + \frac{-6.0}{-2\times23.06} - \frac{1.986\times10^{-3}\times298}{2\times23.06} ln\left(\frac{200\times100^{2}}{20\times10^{2}}\right) = -1.10 \text{ V vs Fc}^{+/0}$$

The cyclic voltammogram recorded on an unbuffered solution containing 200 mM BnOH and 100 mM Et₃N is shown in Figure S7a, and the cyclic voltammogram recorded on a buffered solution is shown in Figure S7b. Conducting measurements under buffered conditions results in a decrease in k_{obs} and a 50 mV increase in apparent overpotential.



Figure S7. Determination of overpotential for BnOH oxidation with $[Ni(PtBu_2NtBu_2)(MeCN)_2][BF_4]_2$. The CV of 0.4 mM $[Ni(PtBu_2NtBu_2)(MeCN)_2][BF_4]_2$ is shown in black. The CV of a catalytic reaction mixture containing 200 mM BnOH and 100 mM Et₃N is shown in red on the left, and the CV of a corresponding buffered solution containing 200 mM BnOH, 20 mM PhCHO, 100 mM Et₃N, and 10 mM $[Et_3NH][BF_4]$ is shown in blue on the right. CVs were recorded in 0.1 M NBu₄BF₄ in MeCN at a scan rate of 100 mV/s.

Oxidation of 2-propanol

For a 1:1 solution of 2-propanol to acetone and triethylamine to triethylammonium, the equilibrium potential is given by:

$$E^{\circ'}{}_{Me2CO/iPrOH (org)} = E^{\circ}{}_{H^{+}/H_{2} (Fc^{+/0})} - 0.0592^{*}pK_{a}(Et_{3}NH^{+}) + \frac{\Delta G^{\circ}{}_{+H_{2} (g)}}{-2F}$$
$$E^{\circ'}{}_{Me2CO/iPrOH (org)} = -0.028 - 0.0592^{*}18.8 + \frac{-4.9}{-2\times23.06} = -1.03 \text{ V vs Fc}^{+/0}$$

Oxidation of 2-propanol under buffered conditions was performed on a solution containing 200 mM 2-propanol, 200 mM acetone, 100 mM triethylamine, and 10 mM triethylammonium tetrafluoroborate. The equilibrium potential under these conditions is calculated as follows:

$$E^{\circ}{}^{\prime}{}_{\text{Me2CO/iPrOH (org)}} = E^{\circ}{}_{\text{H}^{+}/\text{H}_{2} (\text{Fc}^{+/0})} - 0.0592 \text{*}pK_{a}(\text{Et}_{3}\text{NH}^{+}) + \frac{\Delta G^{\circ}{}_{\text{+H}_{2} (g)}}{-2F} - \frac{RT}{2F} \ln \left(\frac{\left[\text{ }^{\text{i}}\text{PrOH} \right] [\text{Et}_{3}\text{N}]^{2}}{\left[\text{Me}_{2}\text{CO} \right] [\text{Et}_{3}\text{NH}^{+}]^{2}} \right)$$
$$E^{\circ}{}^{\prime}{}_{\text{Me2CO/iPrOH (org)}} = -0.028 - 0.0592 \text{*}18.8 + \frac{-4.9}{-2 \times 23.06} - \frac{1.986 \times 10^{-3} \times 298}{2 \times 23.06} \ln \left(\frac{200 \times 100^{2}}{200 \times 10^{2}} \right) = -1.09 \text{ V vs Fc}^{+/0}$$



Figure S8. Determination of overpotential for ⁱPrOH oxidation with $[Ni(P^{tBu}_2N^{tBu}_2)(MeCN)_2][BF_4]_2$. The CV of 0.4 mM $[Ni(P^{tBu}_2N^{tBu}_2)(MeCN)_2][BF_4]_2$ is shown in black. The CV of a catalytic reaction mixture containing 200 mM ⁱPrOH and 100 mM Et₃N is shown in red on the left, and the CV of a corresponding buffered solution containing 200 mM ⁱPrOH, 200 mM Me₂CO, 100 mM Et₃N, and 10 mM [Et₃NH][BF₄] is shown in blue on the right. CVs were recorded in 0.1 M NBu₄BF₄ in MeCN at a scan rate of 50 mV/s.

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