Making a Splash in Homogeneous CO₂ Hydrogenation: Elucidating the Impact of Solvent on Catalytic Mechanisms

Eric S. Wiedner* and John C. Linehan[a]
Abstract: Molecular catalysts for hydrogenation of CO₂ are widely studied as a means of chemical hydrogen storage. Catalysts are traditionally designed from the perspective of controlling the ligands bound to the metal. In recent years, studies have shown that the solvent can also play a key role in the mechanism of CO₂ hydrogenation. A prominent example is the impact of the solvent on the thermodynamic hydride donor ability, or hydricity, of metal hydride complexes relative to the hydride acceptor ability of CO₂. In some cases, simply changing from an organic solvent to water can reverse the direction of hydride transfer between a metal hydride and CO₂. Additionally, the solvent can impact catalysis by converting CO₂ into carbonate species, as well as activate intermediate products for hydrogenation to more reduced products. By understanding the substrate and product speciation, as well as the reactivity of the catalyst towards the substrate, the solvent can be used as a central design component for the rational development of new catalytic systems.

1. Introduction

In recent years, CO₂ has been intensely studied as a potential energy vector for storage of “green” hydrogen that is obtained from renewable energy sources, such as wind and solar. Formic acid, one of the simplest products of CO₂ reduction, has greater energy density than pressurized H₂ storage tanks. As is typical for inert molecules, reaction of CO₂ with H₂ requires a catalyst in order to occur at an appreciable rate. In industrial settings, CO₂ can be hydrogenated to MeOH using heterogeneous catalysts. However, the industrial processes for CO₂ conversion require large centralized facilities that operate with high temperatures and pressures, making them unamenable to small-scale decentralized conversion of CO₂ using geographically dispersed renewable energy sources.

Molecular transition metal catalysts offer several advantages over heterogeneous catalysts. First, molecular catalysts can often hydrogenate CO₂ at mild temperatures and pressures that are compatible with using CO₂ as an energy vector for chemical storage of renewable energy. Second, the performance of molecular catalysts can be rationally controlled through ligand modification. A prominent catalyst design strategy is to promote metal-ligand cooperativity, where the ligand is actively involved in making and breaking bonds during catalysis. For example, functional groups in the second-coordination sphere of the ligand can assist in deprotonation of metal dihydrogen complexes and promote hydride transfer to CO₂.

In addition to the catalyst structure, the solvent can also play a critical role in determining catalytic reactivity. Solvent-dependent catalysis was observed in one of the earliest reports on CO₂ hydrogenation by molecular catalysts, where small amounts of water as a co-solvent were found to accelerate the rate of formic acid production. Since this early study, CO₂ hydrogenation has been performed in a diverse array of solvents and conditions. Often the selection of one solvent over another results from either empirical optimization or specific technological considerations, such as: (1) molecular catalysts are typically more soluble in organic solvents than in water, (2) use of supercritical CO₂ as the solvent greatly facilitates product separation and increases the solubility of H₂, and (3) water is commonly viewed as the ultimate green solvent.

The solvent also plays a fundamental role in determining the free energy profile for reaction of the catalyst with CO₂. Recent years have seen an increase in the mechanistic understanding of how the solvent can influence the mechanism and energetics of CO₂ reduction. This Minireview focuses specifically on recent advances in addressing fundamental mechanistic questions regarding the role of solvent on CO₂ reduction. Many of the details surrounding the various interactions between catalyst and solvent have yet to be resolved, and it is likely that additional roles will be discovered in the future. Accordingly, the goal of this Minireview is not to provide conclusive answers to specific mechanistic issues. Rather, by identifying the current state of knowledge, we seek to provide a basis for future mechanistic studies and promote the use of solvent as an integral, and quantifiable, component of rational catalyst design.

Hydride donor ability, or hydricity, is a thermodynamic parameter that is central to many of the studies described in this Minireview. Hydricity is defined as a heterolytic bond cleavage resulting in the formation of free H⁺, with a corresponding free energy value represented by ΔG°ₘ⁺ [Equation (1)]. The reverse reaction, attack of free H⁺ on an acceptor molecule, corresponds to the hydride acceptor ability of a molecule [Equation (2)]. Hydride acceptor ability is often noted as -ΔG°ₘ⁻ that is, the negative of the hydricity. However, in some sections of this manuscript the hydride acceptor ability will be referred to as ΔG°ₘ⁻ for clarity of discussion. Free H⁺ is a very high energy species and is not a likely intermediate during hydride transfer from one compound to another. However, similar to H⁺ and H transfers, knowledge of the hydricity of two compounds allows one to predict the direction and magnitude of the hydride transfer equilibrium. Miller and Appel reported a comprehensive review on the thermodynamic hydricity of tran-
sition metal hydrides, and Kubiak recently reported an overview of the role of hydricity in CO$_2$ reduction. \(^7\)

\[
\begin{align*}
\text{R-H} & \rightarrow \text{R}^+ + \text{H}^- \quad \Delta G^\circ_{\text{H-}} \quad \text{(1)} \\
\text{R}^+ + \text{H}^- & \rightarrow \text{R-H} \quad \Delta G^\circ_{\text{H-acc}} \quad \text{(2)}
\end{align*}
\]

### 2. Hydride Transfer to CO$_2$

One of the most significant developments in CO$_2$ hydrogenation in recent years has been the recognition that the thermodynamics for hydride transfer from a metal hydride complex to CO$_2$ are remarkably more favorable upon moving from organic solvent to water. This solvent effect is readily quantified by considering the hydricity of the metal hydride and formate. \(^7\)

As shown in Scheme 1, hydride transfer to CO$_2$ will be thermodynamically favorable if the metal hydride is more hydridic than formate. Creutz and co-workers were the first to demonstrate this effect for [HRu(C$_6$Me$_6$)(bpy)]$^+$: hydride transfer from this complex to CO$_2$ is uphill by 10 kcal mol$^{-1}$ in acetonitrile, \(^9\) but downhill by $-3.9$ kcal mol$^{-1}$ in water. \(^8\) Since the pioneering work of Creutz, other metal hydride systems have been discovered where the simple act of moving from an organic solvent to water causes hydride transfer to CO$_2$ to become thermodynamically possible. To date, this solvent effect has been demonstrated for [HFe$_4$(N)(CO)$_{12}$]$^+$, \(^11\) [HNi(diphenylphosphine)$_2$]$^+\) and [{(H)$_2$Co(dmpe)$_2$}]$^+$, \(^13\) as shown in Figure 1.

Several notable reports underscore the impact of solvent-dependent hydricity on the design of catalysts for CO$_2$ reduction. Berben reported solvent-dependent product selectivity for electrocatalytic reduction of CO$_2$ using the iron cluster [Fe$_4$(N)(CO)$_{12}$]$^+$: high selectivity for formate (96%) was observed in water, \(^11\) while H$_2$ was the major product in acetonitrile. \(^14\)

Mechanistic studies identified a parallel between the product selectivity and hydricity of [HFe$_4$(N)(CO)$_{12}$]$^+$, a key catalytic intermediate. \(^11, 15\) Hydride transfer from [HFe$_4$(N)(CO)$_{12}$]$^+$ to CO$_2$ is exergonic ($-9$ kcal mol$^{-1}$) in water, but endergonic ($+5$ kcal mol$^{-1}$) in acetonitrile (Figure 1). Wiedner and co-workers recently reported that [{(H)$_2$Co(dmpe)$_2$}]$^+$ is an active catalyst for aqueous hydrogenation of CO$_2$ to formate, and operates by a different mechanism in water than in organic solvent. \(^13\)

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**Scheme 1.** Thermochemical cycle for determining the free energy for hydride transfer from a metal hydride complex to CO$_2$. **Figure 1.** Solvent-dependent hydricity ($\Delta G^\circ_{\text{H-}}$) for select metal hydride complexes and formate.

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**Acknowledgments:**

<table>
<thead>
<tr>
<th>Eric Wiedner</th>
<th>John Linehan</th>
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</thead>
<tbody>
<tr>
<td>Received his B.S. in chemistry from the Missouri University of Science and Technology (2004), and his Ph.D. from the University of Michigan (2009). He next moved to Pacific Northwest National Laboratory (PNNL) for a postdoctoral fellowship studying under Dan DuBois (2009–2012), then transitioned to a full-time research scientist in the Catalysis Science group at PNNL. Eric’s scientific interest is in the rational design of molecular catalysts, guided by mechanistic and thermodynamic information of the limiting catalytic intermediates.</td>
<td></td>
</tr>
<tr>
<td>Received his B.S. in chemistry from the San Francisco State University (1981), and his Ph.D. in chemistry from the University of California—Davis (1986). He held a postdoctoral fellowship at Argonne National Laboratory prior to moving to Pacific Northwest National Laboratory in 1987. John’s scientific interest is in understanding how catalysts work, utilizing operando NMR, IR, and XAFS spectroscopies.</td>
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water, the hydricity of [(H)Co(dmpe)]\(^+\) is sufficient to react with CO\(_2\). In organic solvents, however, hydride transfer from [(H)Co(dmpe)]\(^+\) to CO\(_2\) is endergonic, and this intermediate must be deprotonated with a very strong organic base to generate HCo(dmpe)\(_2\), a strong hydride donor.\(^{[16]}\) For both [HF\(_6\)(N)(CO)\(_3\)]\(^-\) and [(H)Co(dmpe)]\(^+\), the favorable impact of water on hydride transfer to CO\(_2\) was critical for catalytic formate production.

Given the key role of solvent-dependent hydricity for some catalysts, it is worthwhile to consider the origin of this solvent effect. Acetonitrile and water differ in both dielectric constant (\(\varepsilon\)) and in hydrogen bonding characteristics, both of which could play an important role in promoting conversion of CO\(_2\) to formate. Insight into this question was provided by Yang, who measured the hydricity of [HNi(DHMPE)]\(^+\) and [HNi(TMEPE)]\(^+\) in CH\(_3\)CN (\(\varepsilon = 38\)), DMSO (\(\varepsilon = 47\)), and H\(_2\)O (\(\varepsilon = 80\), as shown in Figure 2.\(^{[12c,17]}\) Surprisingly, the relevant solvent parameter appears to vary with the complex. In the case of [HNi(TMEPE)]\(^+\), the free energy for hydride transfer is clearly correlated with the solvent dielectric. In contrast, hydride transfer from [HNi(DHMPE)]\(^+\) to CO\(_2\) was equally unfavorable in CH\(_3\)CN and DMSO (+13.5 kcal mol\(^{-1}\)), but less unfavorable in H\(_2\)O (+5.9 kcal mol\(^{-1}\)). Thus, either the solvent dielectric or hydrogen bonding effects can dominate the thermodynamics of hydride transfer to CO\(_2\) depending on the metal hydride complex.

Further insight into the origin of the solvent-dependence on the thermodynamics of hydride transfer can be gained through consideration of kinetic effects, which are much easier to investigate in a range of solvents with varying properties. Meyer investigated solvent-dependent kinetics for reaction of Re(bpy)(CO)\(_2\)H and CO\(_2\) to give Re(bpy)(CO)(HCO\(_2\)), a formate complex.\(^{[18]}\) In this study, the second-order rate constant showed a linear correlation with the solvent dielectric constant (Figure 3a). Ishitani performed a similar study using [Ru(terpy)(bpy)H]\(^+\), but found only a poor correlation between the solvent dielectric constant and the second-order rate constant for hydride transfer to CO\(_2\).\(^{[19]}\) For [Ru(terpy)(bpy)H]\(^+\), the rate constant was found to correlate with the solvent acceptor number (AN), which is a measure of the Lewis acidity of the solvent (in other words, its ability to donate a hydrogen bond).\(^{[20]}\) This correlation with AN can be extended to include the rate constant for reaction of [Ru(terpy)(bpy)H]\(^+\) and CO\(_2\) in water, as measured by Creutz (Figure 3b).\(^{[15a]}\)

The discrepancy between the findings for Re(bpy)(CO)\(_2\)H and [Ru(terpy)(bpy)H]\(^+\) is likely related to the range of solvents employed. Only solvents with low AN were used in the study of Re(bpy)(CO)\(_2\)H\(^{[18]}\) while solvents of higher AN (e.g. H\(_2\)O, MeOH) were used in the studies of [Ru(terpy)(bpy)H]\(^+\).\(^{[15a,16]}\) Dielectric and AN are strongly correlated for solvents without OH groups (or other heteroatom-hydrogen bonds). For weak hydrogen-bond donor solvents, it is difficult to determine whether dielectric or AN has a greater impact on the kinetics of hydride transfer to CO\(_2\). However, hydrogen bonding appears to override the dielectric in high AN solvents such as MeOH.

A growing need in CO\(_2\) hydrogenation is to better understand the correlation between thermodynamics and kinetics of hydride transfer to CO\(_2\). Recent computational\(^{[21]}\) and experimental\(^{[22]}\) studies have demonstrated the presence of a linear free energy relationship (LFER) between the driving force and activation energy for hydride transfer to CO\(_2\). The focus of these studies was on tuning the hydricity of the metal hydride through variation of the electronic and steric properties of the supporting ligands. Similar LFERs likely exist for individual metal hydrides as the solvent is varied. However, such a study has not been reported to date, likely due to in part to the challenge of measuring both hydricity values and kinetics for hydride transfer to CO\(_2\) in multiple solvents. To the best of our

![Figure 2](image2.png)

**Figure 2.** Free energy for hydride transfer to CO\(_2\) versus the solvent dielectric constant for [HNi(DHMPE)]\(^+\) and [HNi(TMEPE)]\(^+\). Dashed lines indicate the least-squares fit, while the solid line for [HNi(DHMPE)]\(^+\) is a guide to the eye to illustrate deviations from the least-squares fit.

![Figure 3](image3.png)

**Figure 3.** Plots of the second order rate constant for H\(^+\) transfer to CO\(_2\) (in log form) versus (a) the solvent dielectric constant and (b) the solvent acceptor number. Dashed lines indicate the least-squares fit.
knowledge, the studies on the thermodynamics and kinetics for reaction of \( [\text{Ru(terpy)(bpy)}\text{H}^+] \) with \( \text{CO}_2 \) in acetonitrile\(^{[25]} \) and water\(^{[24a]} \) come closest to establishing a solvent-based LFER. Additional studies of this system in other solvents are needed to clearly establish a solvent-based LFER for this complex.

In addition to hydride transfer, deprotonation of a metal dihydride (or dihydrogen) complex is also a key step for \( \text{CO}_2 \) hydrogenation and can be substantially influenced by the solvent. This is particularly true for hydrogenation of bicarbonate (\( \text{HCO}_3^- \)), which serves as both the substrate and the base. In a computational study of bicarbonate hydrogenation in alcohol solvents, Ahlquist predicted that the activation energy for deprotonation of the catalyst was inversely correlated to the free energy for solvation of \( \text{HCO}_3^- \).\(^{[23]} \) Thus, catalysis is impeded by stabilizing the base through hydrogen bonding interactions, in direct contrast to the trends observed for generating formate via hydride transfer.

### 3. Role of Carbonates

Moving from organic solvent to water affects the speciation of \( \text{CO}_2 \) in solution due to the formation of inorganic carbonates (\( \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-} \)). When catalytic \( \text{CO}_2 \) hydrogenation is performed in aqueous basic conditions, the concentration of \( \text{HCO}_3^- \) is much greater than the concentration of \( \text{CO}_3^{2-} \). This has led some authors to propose that \( \text{HCO}_3^- \) is the real substrate under catalytic conditions.\(^{[24]} \) In support of this proposal, several studies have demonstrated that \( \text{HCO}_3^- \) can be hydrogenated to formate without any added \( \text{CO}_2 \).\(^{[25]} \) Identification of the true substrate, \( \text{CO}_2 \) or \( \text{HCO}_3^- \), is complicated by the interconversion of these two species in solution (Equation (3)). The first order rate constant for conversion of \( \text{HCO}_3^- \) to \( \text{CO}_2 \) and \( \text{OH}^- \) is 0.7 h\(^{-1} \) at room temperature,\(^{[26]} \) corresponding to \( \Delta G^\circ = 22.5 \text{ kcal mol}^{-1} \). For comparison, one of the fastest reported catalysts for hydrogenation of Na\( \text{HCO}_3^- \), a ruthenium pincer complex, has \( \text{TOF} = 1700 \text{ h}^{-1} \) at 80 °C and 40 bar \( \text{H}_2 \).\(^{[28]} \) The barrier for this catalytic TOF corresponds to \( \Delta G^\circ \approx 21 \text{ kcal mol}^{-1} \), which is similar to the barrier for \( \text{HCO}_3^- \) decomposition into \( \text{CO}_2 \). Thus, it is feasible that the generation of \( \text{CO}_2 \) from \( \text{HCO}_3^- \) may be a major contributor to the rate-determining process of Na\( \text{HCO}_3^- \) hydrogenation.

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \tag{3}
\]

One way to probe the identity of the true substrate is to measure the kinetics of catalysis with and without added \( \text{CO}_2 \). However, few studies report catalysis under conditions that differ by only the \( \text{CO}_2 \) pressure. In a batch reactor study of \( \text{HCO}_3^- \) hydrogenation with the \( [\text{RuCl}_3(\text{C}_3\text{H}_5)_3]\text{H}^+ \) dppm system, more catalytic turnovers were obtained in the presence of 35 bar \( \text{CO}_2 \) (2500 turnovers) than with no added \( \text{CO}_2 \) (2100 turnovers).\(^{[25c]} \) In a recent study using a water-soluble Ni(diisophosphate)\(^{2+} \) complex, catalysis was 5 \times faster with 34 atm of 1:1 \( \text{H}_2: \text{CO}_2 \) than with only \( \text{H}_2 \) and \( \text{HCO}_3^- \).\(^{[12a]} \) While limited in scope, these studies suggest that hydrogenation of \( \text{CO}_2 \) is more facile than direct hydrogenation of \( \text{HCO}_3^- \).

From a thermodynamic standpoint, \( \text{HCO}_3^- \) is a poorer hydride acceptor than \( \text{CO}_2 \). The initial product of \( \text{H}^- \) transfer to \( \text{HCO}_3^- \) would be \( \text{H}_2\text{CO}_3^+ \), a doubly-deprotonated form of orthoformic acid (Scheme 2). This unstable intermediate would rapidly dissociate \( \text{OH}^- \) to give the formate anion. There is insufficient thermochemical data to determine the true hydride acceptor ability of \( \text{HCO}_3^- \) due to the instability of \( \text{H}_2\text{CO}_3^+ \). However, the effective hydride acceptor ability (\( \Delta G^\circ_{\text{H-ac}} \)) of \( \text{HCO}_3^- \), corresponding to \( \text{C}^-\text{H} \) bond formation and \( \text{C}^-\text{O} \) bond cleavage, can be determined using the free energy for conversion of \( \text{HCO}_3^- \) to \( \text{CO}_2 \) (8.4 kcal mol\(^{-1} \) at pH 14 and 1 atm \( \text{CO}_2 \))\(^{[26]} \) and the aqueous hydride acceptor ability of \( \text{CO}_2 \) (−24 kcal mol\(^{-1} \))\(^{[10b]} \) as illustrated in Scheme 2. This effective hydride acceptor ability is pH-dependent due to the presence of \( \text{OH}^- \) in the chemical equilibrium, resulting in \( \Delta G^\circ_{\text{H-ac}} = -34.8 + (1.364 \times \text{pH}) \text{ kcal mol}^{-1} \). At \( \text{pH}_2 = 1 \text{ atm}, \text{HCO}_3^- \) is the better hydride acceptor when \( \text{pH} < 7.8 \), while \( \text{CO}_2 \) is the better hydride acceptor when \( \text{pH} > 7.8 \).

While this section has so far focused on inorganic carbonate (\( \text{HCO}_3^- \)), similar mechanistic questions are relevant for hydrogenation of \( \text{CO}_2 \) that has been captured as an organic carbonate (\( \text{ROCO}_2^- \)) or carbamate (\( \text{R}_2\text{NCO}_2^- \)).\(^{[27]} \) In these studies, \( \text{CO}_2 \) capture is performed at ambient temperature, while the hydrogenation reaction often requires temperatures > 100 °C to drive catalysis at an appreciable rate. Mechanistic studies are needed to determine whether the substrate is \( \text{CO}_2 \) that is released from the organic carbonate (or carbamate) at the high temperatures required for hydrogenation.

### 4. Products of \( \text{CO}_2 \) Hydrogenation

Direct hydrogenation of \( \text{CO}_2 \) to formic acid (\( \text{HCO}_2\text{H} \)) in the absence of a strong base is challenging due to the unfavorable thermodynamics of the reaction. In water, formic acid is +5.0 kcal mol\(^{-1} \) uphill from \( \text{CO}_2 \) and \( \text{H}_2 \) at standard state (25 °C and 1 atm). Reaction conditions must be selected to drive the unfavorable equilibrium to generate significant amounts of formic acid, such as performing catalysis at elevated pressures. Laurenzcy and co-workers reported an intriguing solvent-dependence on formic acid production using \( \text{RuCl}_3(\text{PTA})_3 \) as the catalyst.\(^{[28]} \) With this catalyst, mixtures of DMSO and water gave much higher concentrations of formic acid than other solvents (Figure 4). Several lines of evidence suggested that...
the change in formic acid yield resulted from a change in the equilibrium concentration of formic acid in DMSO. First, the RuCl₃(PTA)₄ catalyst could be recycled multiple times without a loss in activity, indicating the yields of formic acid were not influenced by catalyst decomposition. Second, RuCl₃(PTA)₄ also catalyzed the reverse reaction, dehydrogenation of formic acid.

To further investigate the solvent-dependent catalysis by RuCl₃(PTA)₄, Laurenczy used calorimetry to measure the heat of mixing of formic acid in a wide range of solvents [Equation (4)].²⁹ Importantly, formic acid dissolution became more exothermic as the solvent basicity was increased (Figure 5).

This finding has a direct parallel with solvent donor number, which corresponds to its Lewis basicity.³⁰ This study supports the conclusion that the increased yield of formic acid obtained in DMSO results from improvement in the thermodynamics for the net reaction. The entropy for hydrogenation of CO₂ to formic acid is also likely to vary in different solvents, and future measurements of this thermodynamic parameter would be valuable.

HCO₂H(lq) → HCO₂H(solv) ΔH°ₐ,lq→solv

Sans and Dupont recently demonstrated that increased yields of formic acid could be obtained by hydrogenating CO₂ in an imidazolium ionic liquid using Ru(II)CO₃ as a precata-

lyst.³¹ The highest yields of formic acid (>1 M) were achieved using either acetate or formate as the anion for the ionic liquid. Carboxylic acids, such as formic acid and acetic acid, are known to homoaasociate with their conjugate base in many organic solvents [Equation (5)].³² The improved yields of formic acid are likely driven by hydrogen bonding with the ionic liquid anion.

RCO₂⁺ + R′CO₂⁻ → (RCO₂H-O₂CR′)⁻

Hydrogenation of CO₂ to methanol is an exergonic reaction (∆G° = -5.0 kcal mol⁻¹ in H₂O), yet is very difficult to achieve using molecular catalysts. Indirect methods for obtaining MeOH from CO₂ include tandem catalysts and combined capture and conversion.²⁷ Direct hydrogenation of CO₂ to MeOH has been achieved with Ru(triphos)³⁴ and Co(triphos)³⁵ at high temperatures and pressures. Both of these approaches, indirect and direct conversion, require high temperatures (>130 °C) to obtain MeOH at a reasonable rate. One exception to the requirement of high temperature comes from Himeda and Laurenczy, who showed that direct hydrogenation of CO₂ to MeOH could be achieved at ambient temperature using [Cp*Ir(dhbp)(H₂O)]⁺⁺ (dhbp = 4,4’-dihydroxy-2,2’-bipyridine) as the catalyst in 2 M aqueous H₂SO₄ (pH = 0).³⁶ The acidic conditions were critical for MeOH production, as the same Ir catalyst only produces formic acid at pH 3.³⁷

In a follow-up mechanistic study, Himeda and Laurenczy proposed that protonation of formic acid at low pH activates it to accept a hydride from the catalyst.³⁸ The thermodynamic feasibility of this hypothesis can be checked through determination of the hydride acceptor abilities of both formic acid, HCO₂H, and protonated formic acid, HC(OH)₂⁺ (Figure 6). These values have not been previously reported, but can be readily calculated from literature data. The first step is to deter-

\[
\begin{align*}
\text{HCO}_2\text{H} + 2\text{H}^+ + 2e^- & \rightarrow \text{H}_2\text{CO}_2 + \text{H}_2 \\
\text{E} & = -0.229 \text{V} \\
\Delta G° & = 1.3 \text{ kcal mol}^{-1} \\
\text{H}_2\text{CO}_2 & + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C(OH)}_2 \\
K_w & = 10^5 \\
\Delta G° & = -6.5 \text{ kcal mol}^{-1} \\
\text{H}_2\text{CO}_2 & + 2\text{H}^+ + 2e^- \\
E & = 0 \text{V} \\
\Delta G° & = 0 \text{ kcal mol}^{-1} \\
\text{HCO}_2\text{H} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{C(OH)}_2 \\
\Delta G° & = -4.2 \text{ kcal mol}^{-1}
\end{align*}
\]

Figure 4. Equilibrium concentration of formic acid obtained in different solvents by hydrogenation of CO₂ with RuCl₃(PTA)₄. Conditions: t = 50 °C, P(total) = 100 bar, 1:1 H₂-CO₂, BMIM = 1-butyl-3-methylimidazolium tetrafluoroborate (p-toluene sulfonate).

Figure 5. Heat of mixing of formic acid (ΔH°₁₈₅→liq) in different solvents.

Figure 6. (a) Thermochemical cycle for determining the free energy for hydrogenation of formic acid to methanol in water. (b) Thermochemical Scheme for conversion of formic acid to methanol by sequential transfer of H⁺ and H₂.
mine the free energy for hydrogenation of HCO$_2$H to methanediol, H$_2$C(OH)$_2$, from a thermodynamic cycle that includes the standard potential for reduction of HCO$_2$H to formaldehyde, H$_2$CO,$^{[29]}$ the equilibrium constant for hydration of H$_2$CO to give H$_2$C(OH)$_2$,$^{[40]}$ and the standard potential of the H$^+$/H$_2$ couple, that is, the SHE electrode (Figure 6a). This cycle affords $\Delta G^\circ = -4.2$ kcal mol$^{-1}$ for hydrogenation of HCO$_2$H to H$_2$C(OH)$_2$. This value can be combined with literature $p_k$ values, along with the constant for heterolytic cleavage of H$_2$,$^{[106]}$ to determine the desired hydride acceptor abilities (Figure 6b). For example, the $p_K$ of H$_2$C(OH)$_2$ in water is reported to be 13.3,$^{[41]}$ which leads to a hydride acceptor ability of $-20$ kcal mol$^{-1}$ for formic acid. Similarly, protonated acetic acid, CH$_3$C(OH)$_2^+$, has been reported to have a $p_K$ of $-6$ in water.$^{[42]}$ Using this $p_K$ as a proxy for that of HCO$_2$H,$^{2}$ affords a hydride acceptor ability of $-47$ kcal mol$^{-1}$ for HC(OH)$_2^+$. Based on this thermodynamic analysis, hydride transfer from [Cp$^{\text{Ir}}$(dhbb)(H$_2$O)]$^{2+}$ ($\Delta G^\circ_{111} \approx 31$ kcal mol$^{-1}$)$^{[43]}$ to HCO$_2$H is endergonic ($\approx 11$ kcal mol$^{-1}$), while hydride transfer to HC(OH)$_2^+$ is exergonic ($\approx 16$ kcal mol$^{-1}$). These data suggest HC(OH)$_2^+$ is the actual hydride acceptor in acidic conditions, in support of the mechanistic proposal from Himeda and Laurenczy. Yang reached the opposite mechanistic conclusion in a recent computational analysis, in which the barrier for hydride transfer to HCO$_2$H was calculated to be 9 kcal mol$^{-1}$ lower than for hydride transfer to HC(OH)$_2^+$. Clearly further experimental and computational studies are needed to resolve the mechanistic consequences of performing catalysis in highly acidic conditions.

5. Summary and Outlook

This article describes both recent and emerging mechanistic studies regarding the impact of solvent on the mechanisms for hydrogenation of CO$_2$ by molecular catalysts. Changing solvent conditions can affect the thermodynamics and kinetics for hydride transfer from the catalyst to CO$_2$. Carbonate species, both inorganic and organic, affects the speciation of CO$_2$ and allows the possibility of multiple hydride transfer pathways. Additionally, the solvent can be used lower the thermodynamic barrier for hydrogenation of CO$_2$ to formic acid, as well as enable the formation of methanol by activating formic acid to didehydrogen. This allows the possibility for multiple hydride transfer pathways.

Further mechanistic understanding is needed to be able to use the solvent as a key parameter for rational control over catalyst performance.

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Conflict of interest

The authors declare no conflict of interest.

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