



Homogeneous Catalysis

Changing the Mechanism for CO₂ Hydrogenation Using Solvent-Dependent Thermodynamics

Samantha A. Burgess, Aaron M. Appel, John C. Linehan, and Eric S. Wiedner*

Abstract: A critical scientific challenge for utilization of CO_2 is the development of catalyst systems that function in water and use inexpensive and environmentally friendly reagents. We have used thermodynamic insights to predict and demonstrate that the $HCo^1(dmpe)_2$ catalyst system, previously described for use in organic solvents, can hydrogenate CO_2 to formate in water with bicarbonate as the only added reagent. Replacing tetrahydrofuran as the solvent with water changes the mechanism for catalysis by altering the thermodynamics for hydride transfer to CO_2 from a key dihydride intermediate. The need for a strong organic base was eliminated by performing catalysis in water owing to the change in mechanism. These studies demonstrate that the solvent plays a pivotal role in determining the reaction thermodynamics and thereby catalytic mechanism and activity.

Conversion of CO₂, an inexpensive and abundant resource, into a chemical fuel or carbon feedstock could help to reduce our dependence on fossil fuels.^[1] Hydrogenation of CO₂ to formate using a molecular transition-metal catalyst is typically performed in an organic solvent using stoichiometric organic base.^[2] Due to environmental considerations, water is more desirable as a solvent. Catalysts based on precious metals (Ir,^[3] Ru,^[4] Rh^[5]) and base-metals (Co,^[6] Fe,^[7] Ni^[8]) have been reported for hydrogenation of CO₂ in water (Figure 1). Herein, we report that $(H)_2 Co^{III} (dmpe)_2^+ (dmpe =$ 1,2-bis(dimethylphosphino)ethane) is a catalyst for hydrogenation of CO₂ to formate in water using sodium bicarbonate as the base. The turnover frequency (TOF) of (H)₂Co^{III}- $(dmpe)_2^+$ is among the highest reported for a base-metal catalyst operating in water. Notably, water plays a critical role in the catalytic mechanism by enabling hydride transfer to CO_2 from $(H)_2Co^{III}(dmpe)_2^+$ instead of $HCo^I(dmpe)_2$, as is observed in organic solvents. This change eliminates the need for a strong organic base to regenerate the catalyst.

In previous studies, we used existing thermochemical data^[9] to predict that hydride transfer from HCo^I(dmpe)₂ to CO₂ would be downhill by -8 kcal mol^{-1} in organic solvents.^[10] The key to achieving fast catalysis was to use Verkade's superbase (p K_a^{MeCN} = 33.6 for the conjugate acid)^[11] to deprotonate the weakly acidic dihydride intermediate, (H)₂Co^{III}(dmpe)₂⁺ (p K_a^{MeCN} = 33.7), thereby regen-



Figure 1. Previously reported base-metal catalysts for $\rm CO_2$ hydrogenation in water and the cobalt catalyst described in this work.

erating the active hydride donor, $HCo^{I}(dmpe)_{2}$. With a TOF of 3400 h⁻¹ at 21 °C and 1 atm of H_{2}/CO_{2} , $HCo^{I}(dmpe)_{2}$ remains the fastest catalyst for hydrogenation of CO_{2} to formate under ambient conditions.

We initially avoided studying $HCo^{I}(dmpe)_{2}$ in water, as it is rapidly protonated by water to give $(H)_{2}Co^{III}(dmpe)_{2}^{+}$ (see below). In organic solvents, hydride transfer from $(H)_{2}Co^{III}$ - $(dmpe)_{2}^{+}$ to CO_{2} is estimated to be uphill by 10 kcalmol⁻¹ (Supporting Information). Recent studies have shown that water exhibits a favorable effect on hydride transfer to CO_{2} when contrasted with organic solvents.^[8,12] This solvent effect arises from the stabilization of formate by hydrogen-bonding in water.^[12c] Several metal hydride complexes have been identified for which hydride transfer to CO_{2} is endoergic in organic solvent, but exoergic in water. These findings prompted us to reinvestigate the activity of $(H)_{2}Co^{III}(dmpe)_{2}^{+}$ for hydrogenation of CO_{2} using water as a solvent.

The hydride donor ability, or hydricity (ΔG°_{H-}), of a catalyst is a critical parameter for determining whether the catalyst will transfer a hydride to CO₂.^[13] A hydricity of 23 kcal mol⁻¹ can be estimated for (H)₂Co^{III}(dmpe)₂⁺ in water by using empirical thermodynamic scaling relationships of metal hydride complexes (Supporting Information). This hydricity suggests that transfer of a hydride from (H)₂Co^{III}-(dmpe)₂⁺ to CO₂ in water will be slightly favorable at 25 °C and 1 atm, as the hydricity of formate is 24.1 kcal mol⁻¹ in water.^[14]

Taking this estimated hydricity as a guide, we examined the catalytic activity of $(H)_2 Co^{III} (dmpe)_2^+$ in water with a bicarbonate buffer. Using operando NMR spectroscopy in custom high-pressure PEEK cells,^[15] we observed slow catalysis at room temperature (ca. 1 h⁻¹) and modest turnovers at 100 °C. An initial TOF of 560(160) h⁻¹ was measured for hydrogenation of CO₂ to formate using $(H)_2 Co^{III} (dmpe)_2^+$

^[*] Dr. S. A. Burgess, Dr. A. M. Appel, Dr. J. C. Linehan, Dr. E. S. Wiedner Catalysis Science Group, Pacific Northwest National Laboratory P.O. Box 999, Richland, WA 99352 (USA) E-mail: eric.wiedner@pnnl.gov

Supporting information and the ORCID identification number(s) for
 the author(s) of this article can be found under: https://doi.org/10.1002/anie.201709319.

(0.028 mM) in H₂O with 0.8M NaHCO₃ at 100 °C and 34 atm of a 1:1 mixture of H₂ and CO₂ (Figure 2). Under these conditions, about 7700 turnovers (mol of formate per mol of (H)₂Co^{III}(dmpe)₂⁺) were obtained in 67 h. Table 1 shows a comparison of the catalytic activity of (H)₂Co^{III}(dmpe)₂⁺ versus other base-metal catalysts reported for hydrogenation of CO₂ in water. The TOF of (H)₂Co^{III}(dmpe)₂⁺ is comparable to the fastest base-metal catalysts, and the number of turnovers by (H)₂Co^{III}(dmpe)₂⁺ is 10-fold larger than the next best catalytic system, Fe(PNP)(H₂)₂CO.^[7a]

Dissolution of $HCo^{I}(dmpe)_{2}$ in water (pH 8.6) results in rapid protonation and complete conversion to (H)₂Co^{III}-(dmpe)₂⁺, as identified by comparison of the ¹H and ³¹P{¹H} NMR spectra with an authentic sample dissolved in H₂O (Figure 3 a,b). (H)₂Co^{III}(dmpe)₂⁺ retains a *cis* geometry in



Figure 2. Kinetic plot showing the formate concentration versus time at 100 °C in H₂O with 34 atm of 1:1 H₂/CO₂, 0.028 mM (H)₂Co^{III}-(dmpe)₂⁺, and 0.8 M NaHCO₃. The formate concentration was determined using operando ¹H NMR spectroscopy by integrating the formate resonance relative to an internal standard. The initial TOF was measured from the best linear fit line (R^2 =0.98).

Table 1: Comparison of the catalytic activity for hydrogenation of CO_2 to formate in water using different base-metal complexes.

Catalyst	P _{total} [atm] ^[a]	Т [°С]	TOF $[h^{-1}]^{[b]}$	Turnovers	Ref.
(H) ₂ Co(dmpe) ₂ ⁺	34	100	560	7700	this work
$Ni(L)_{2}^{2+[c]}$	34	100	0.6	16	[8]
Cp*Co(bpyOH) ^{2+[d]}	34	100	39	39	[6]
$Fe(PNP)(H)_2CO^{[e,f]}$	9.9 ^[g]	80	160	790	[7a]

[a] Total pressure of 1:1 H_2/CO_2 at room temperature. [b] Initial TOF. [c] L=1,2-[bis(dimethoxypropyl)phosphino]ethane. [d] bpyOH=4,4'dihydroxyl-2,2'-bipyridine. [e] PNP=2,6-bis[(di-*tert*-butylphosphino)methyl]pyridine. [f] 9% (ν/ν) of tetrahydrofuran as a co-solvent. [g] 2:1 H_2/CO_2 .



Figure 3. a) ¹H NMR spectrum of *cis*-(H)₂Co^{III}(dmpe)₂⁺ in H₂O showing the hydride region. b) ³¹P{¹H} NMR spectrum of *cis*-(H)₂Co^{III}- (dmpe)₂⁺ in H₂O. c) ¹H NMR spectrum of *trans*-HCo^{III}(dmpe)₂(OH)⁺ in H₂O showing the hydride region. d) ³¹P{¹H} NMR spectrum of *trans*-HCo^{III}(dmpe)₂(OH)⁺ in H₂O.

water, as supported by the appearance of two broad resonances in the ³¹P{¹H} NMR spectrum. A new complex with a hydride resonance at -32.9 ppm in the ¹H NMR spectrum is observed when (H)₂Co^{III}(dmpe)₂⁺ is dissolved in MES^[16] buffer (Figure 3 c). This hydride resonance is significantly upfield from that of (H)₂Co^{III}(dmpe)₂⁺ (-14.5 ppm). The ³¹P{¹H} NMR spectrum of this new complex contains a broad singlet at 54.2 ppm (Figure 3 d), indicating all four phosphorus atoms are magnetically equivalent. Comparison of these NMR resonances to closely related Fe analogues^[17] suggests this new species is *trans*-HCo^{III}(dmpe)₂(OH)⁺, with a hydroxide ligand *trans* to a hydride ligand.

Only three cobalt species were observed by NMR spectroscopy during catalysis. Two species, $(H)_2Co^{III}(dmpe)_2^+$ and $HCo^{III}(dmpe)_2(OH)^+$, are observed at the start of catalysis and persist during the first 5 h of catalysis, the time period over which the initial TOF was measured. After about 2 h of catalysis, a new species appears as a singlet at 50 ppm in the ³¹P{¹H} NMR spectrum, and is the only species observed after 10 h of catalysis. A hydride resonance was not observed in the ¹H NMR spectrum of this species, suggesting it is not a cobalt hydride complex. The identity of this complex is not known and is still being investigated.

To determine the aqueous hydricity of $(H)_2 Co^{III}(dmpe)_2^+$, it was equilibrated with $HCo^{III}(dmpe)_2(OH)^+$ at 25 °C in MES buffer under 1 atm H₂. A hydricity of $\Delta G^{\circ}_{H^-} = 14.0(3)$ kcalmol⁻¹ was calculated for $(H)_2 Co^{III}(dmpe)_2^+$ using the measured equilibrium constant, the free energy for autoionization of H₂O, and the free energy for heterolytic cleavage of H₂ in water^[14] (Scheme 1). This hydricity corre-

$$(H)_{2}Co^{III}(dmpe)_{2}^{+} + H_{2}O \longrightarrow HCo^{III}(dmpe)_{2}(OH)^{+} + H_{2} -1.364 \log(K_{eq})$$

$$H^{+} + OH^{-} \longrightarrow H_{2}O -1.364 \log(10^{14})$$

$$H_{2} \longrightarrow H^{+} + H^{-} 34.2$$

$$(H)_{2}Co^{III}(dmpe)_{2}^{+} + OH^{-} \longrightarrow HCo^{III}(dmpe)_{2}(OH)^{+} + H^{-} \Delta G^{\circ}_{H^{-}}$$

$$\Delta G^{\circ}_{H^{-}} = \Delta G^{\circ}_{H^{-}} + 1.364(14-pH)$$

Scheme 1. Thermochemical cycle for determining the hydricity of $(H)_2Co^{III}(dmpe)_2^+$, with units of kcal mol⁻¹.

Angew. Chem. Int. Ed. 2017, 56, 15002-15005

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sponds to a standard state of $[OH^-] = 1M$ due to the binding of hydroxide to cobalt. The effective hydricity $(\Delta G^{\text{eff}}_{\text{H}-})$ of $(\text{H})_2\text{Co}^{\text{III}}(\text{dmpe})_2^+$ is pH-dependent due to the change in concentration of OH⁻. At pH 7, the effective hydricity of $(\text{H})_2\text{Co}^{\text{III}}(\text{dmpe})_2^+$ is 23.5 kcal mol⁻¹, which is in excellent agreement with the hydricity estimated from scaling relationships (23 kcal mol⁻¹).

Formate has a hydricity of 24.1 kcalmol⁻¹ in water.^[14] Consequently, hydride transfer from $(H)_2Co^{III}(dmpe)_2^+$ to CO₂ is exoergic when pH > 6.6 at 25 °C and 1 atm of CO₂. In the hydricity measurements described above, HCo^{III}(dmpe)₂-(OH)⁺ is stable towards H₂ formation at pH 6.5, indicating the effective hydricity of HCo^{III}(dmpe)₂(OH)⁺ is greater than 27 kcalmol⁻¹. Therefore, hydride transfer to CO₂ is thermodynamically more favorable for $(H)_2Co^{III}(dmpe)_2^+$ than for HCo^{III}(dmpe)₂(OH)⁺ by at least 3 kcalmol⁻¹. This reactivity trend is expected to hold under catalytic conditions of 100 °C and 17 atm of CO₂.

The proposed mechanisms for CO₂ hydrogenation using $HCo^{I}(dmpe)_{2}$ in tetrahydrofuran^[10] and $(H)_{2}Co^{III}(dmpe)_{2}^{+}$ in water are shown in Scheme 2. The two cycles diverge from a common intermediate, $(H)_2 Co^{III} (dmpe)_2^+$. In the aqueous mechanism, a hydride is transferred from $(H)_2 Co^{III} (dmpe)_2^+$ to CO₂ to give formate and a coordinatively unsaturated intermediate, which rapidly binds HO⁻ yielding HCo^{III}- $(dmpe)_2(OH)^+$. An unobserved dihydrogen compound, $HCo^{III}(dmpe)_2(H_2)^{2+}$, is likely formed by loss of HO^- from $HCo^{III}(dmpe)_2(OH)^+$. We have not been able to independently generate HCo^{III}(dmpe)₂(H₂)²⁺, however, isoelectronic Fe and Mn analogues are known.^[18] Deprotonation of this proposed intermediate completes the catalytic cycle by regenerating $(H)_2 Co^{III} (dmpe)_2^+$. This cycle is thought to be the dominant pathway for production of formate during the first several hours of catalysis. A second cycle may be operative over longer periods of catalysis, as no hydride species are observed by operando NMR spectroscopy after 5 h.

In contrast to the CoI/CoIII mechanism for catalysis in tetrahydrofuran, the oxidation state of cobalt for the aqueous catalysis is proposed to remain Co^{III}. No reaction was observed when (H)₂Co^{III}(dmpe)₂⁺ is heated at 80°C in $[D_8]$ THF under CO₂ (1 atm), suggesting either a thermodynamic or kinetic barrier to hydride transfer in this solvent. A cobalt(III) monohydride complex, HCo^{III}(dmpe)₂(CH₃CN)²⁺, was prepared by reaction of $(H)_2 Co^{III} (dmpe)_2^+$ with 2,6dimethylpyridinium in acetonitrile. Reaction of HCoIII- $(dmpe)_2(CH_3CN)^{2+}$ with 3 equiv of cesium formate generates a mixture of $(H)_2Co^{III}(dmpe)_2^+$ and a new species that is tentatively assigned as a hydride-formate complex, HCo^{III}- $(dmpe)_2(O_2CH)^+$. These data indicate that hydride transfer from $(H)_2 Co^{III} (dmpe)_2^+$ to CO_2 is thermodynamically unfavorable in organic solvents, and that water as a solvent is critical for activating the Co^{III}-pathway for catalysis.

A benefit of the aqueous Co^{III} -pathway is that a strong base is not required to deprotonate the putative HCo^{III} - $(dmpe)_2(H_2)^{2+}$ intermediate. This species is estimated to be 25 pK_a units less acidic than $(H)_2Co^{III}(dmpe)_2^+$ in organic solvent using the ligand additivity method.^[19]

In summary, we have shown that $(H)_2 Co^{III} (dmpe)_2^+$ is an active catalyst for the hydrogenation of CO₂ to formate in water with NaHCO₃ as an inexpensive base. We observe that catalysis operates by a different mechanism in water than in tetrahydrofuran due to the improved thermodynamics for hydride transfer from $(H)_2 Co^{III} (dmpe)_2^+$ to CO₂ in water. As a result of the change in the mechanism, we were able to avoid the strong and expensive Verkade's superbase utilized for CO₂ hydrogenation with HCo¹ (dmpe)₂ in tetrahydrofuran.^[10] Further mechanistic studies of this catalyst system are currently underway.



Scheme 2. Previously reported catalytic cycle for CO_2 hydrogenation using $HCo^1(dmpe)_2$ in tetrahydrofuran (left)^[10] and proposed catalytic cycle for CO_2 hydrogenation with $(H)_2Co^{[1]}(dmpe)_2^+$ in water (right).

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Acknowledgements

The research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. The authors thank Dr. Katarzyna Grubel for X-ray crystallographic analysis. Pacific Northwest National Laboratory is operated by Battelle for DOE.

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon dioxide fixation · homogeneous catalysis · hydricity · hydrogenation · solvent effects

How to cite: Angew. Chem. Int. Ed. 2017, 56, 15002–15005 Angew. Chem. 2017, 129, 15198–15201

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Manuscript received: September 8, 2017 Accepted manuscript online: September 29, 2017 Version of record online: October 23, 2017