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A Cobalt-Based Catalyst for the Hydrogenation of CO_2 under Ambient Conditions

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Ⓢ *Supporting Information*

ABSTRACT: Because of the continually rising levels of CO_2 in the atmosphere, research for the conversion of CO_2 into fuels using carbon-neutral energy is an important and current topic in catalysis. Recent research on molecular catalysts has led to improved rates for conversion of CO_2 to formate, but the catalysts are based on precious metals such as iridium, ruthenium and rhodium and require high temperatures and high pressures. Using established thermodynamic properties of hydricity (ΔG_{H^-}) and acidity (pK_a), we designed a cobalt-based catalyst system for the production of formate from CO_2 and H_2. The complex $Co(dmpe)_2H$ (dmpe is 1,2-bis(dimethylphosphino)ethane) catalyzes the hydrogenation of CO_2, with a turnover frequency of 3400 h^{-1} at room temperature and 1 atm of 1:1 $CO_2{:}H_2$ (74 000 h^{-1} at 20 atm) in tetrahydrofuran. These results highlight the value of fundamental thermodynamic properties in the rational design of catalysts.

The rise in average global surface temperatures and atmospheric CO_2 concentrations continue to drive research on the storage of carbon-neutral energy, such as that from wind and solar.[1,2] While the economics of collecting energy from these sources are improving, the storage of energy from these intermittent energy sources remains an impediment for large scale utilization. Storing energy in chemical bonds through the conversion of inexpensive substrates to fuels is one route to enabling the storage of carbon-neutral energy; however, the widespread use of this approach will require the development of catalysts based upon abundant metals.[3] The production of hydrogen is one possible route, but it provides challenges, especially for transportation.[4] Alternatively, the reduction of CO_2 can be performed either directly with protons and electrons[5−8] or through the carbon-neutral production of H_2 and subsequent hydrogenation of CO_2,[9−14] as in eq 1.

$$H_2 + CO_2 + \text{base} \rightleftharpoons HCO_2^- + \text{base} - H^+ \qquad (1)$$

We previously demonstrated that nickel-based electrocatalysts are effective for converting formate into protons and electrons, eq 2, allowing the recovery of energy from formate using catalysts containing a first-row transition metal.[15,16]

$$HCO_2^- \rightarrow H^+ + 2e^- + CO_2 \qquad (2)$$

In the present case, the storage of energy in a carbon−hydrogen bond is performed by hydrogenation of CO_2.[17,18]

Using thermodynamic parameters of hydricity (ΔG_{H^-}) and acidity (pK_a) as guides, we developed a new first row catalyst system with high catalytic activity even under ambient conditions. For the design of a new formate production catalyst system, we considered a catalytic cycle containing three essential reactions: (A) a hydride transfer from a metal complex to CO_2, (B) addition of H_2 to the resulting metal complex, and (C) the regeneration of the metal hydride complex by deprotonation, steps A, B, and C, respectively, in Figure 1. In order to obtain catalytic results at room temperature and pressure, the energetics of the reactions in steps A and C (Figure 1) needed to be well matched in the catalyst system.

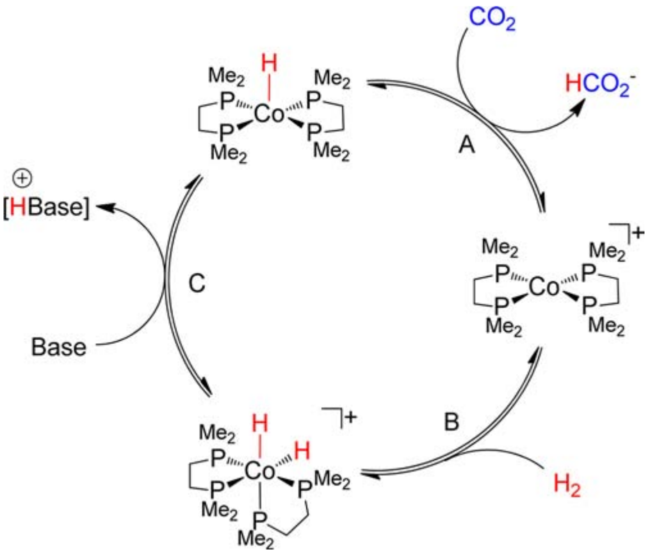

Figure 1. Proposed catalytic cycle for CO_2 hydrogenation using $Co(dmpe)_2H$.

Hydride donor abilities, or the free energy for cleaving H^- from a metal hydride, have been characterized for a range of complexes using both experimental and computational approaches. Rhodium and iridium based phosphine catalysts are better hydride donors than the respective cobalt phosphines, having hydricities significantly lower than the 44 kcal/mol required for the direct hydride transfer to CO_2.[19,20] However, improving the hydride donating ability of the monohydride increases the strength of the base needed to deprotonate the dihydride cation, step C, to complete the

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catalytic cycle.[21,22] If either one of these steps is substantially mismatched in energy, catalysis will be impeded and may require elevated temperatures and/or pressures. Thus, because the two trends work in opposition of one another, the challenge comes in finding a system that can both (1) transfer a hydride to CO_2 and (2) form a dihydride cation that is sufficiently acidic to be deprotonated.

Using chelating diphosphine ligands, the hydride donor abilities ($M-H \rightarrow M^+ + H^-$) of metal complexes can be controlled, including those for complexes of cobalt and rhodium.[23,24] The cobalt−hydride bis-diphosphine complex $Co(dmpe)_2H$ (where dmpe is 1,2-bis(dimethylphosphino)-ethane)[25] has a sufficiently weak heterolytic M−H bond (ΔG_{H^-}) to react with CO_2 to produce formate, as in eqs 3−5 (for which the values are free energies in acetonitrile). The energetics for the overall reaction are defined by the difference in the heterolytic bond strengths of $Co(dmpe)_2H$[22,24,26] and formate,[19,20] eqs 3 and 4, respectively. The overall reaction has a free energy of −8 kcal/mol for the transfer of a hydride, eq 5 as well as step A in the catalytic cycle in Figure 1.

$$Co(dmpe)_2H \rightarrow Co(dmpe)_2{}^+ + H^- \qquad \Delta G_{H^-} = +36\ \text{kcal/mol} \tag{3}$$

$$CO_2 + H^- \rightarrow HCO_2{}^- \qquad -\Delta G_{H^-} = -44\ \text{kcal/mol} \tag{4}$$

$$Co(dmpe)_2H + CO_2 \rightarrow Co(dmpe)_2{}^+ + HCO_2{}^- \qquad \Delta G_{H^-} = -8\ \text{kcal/mol} \tag{5}$$

Equally important for the overall catalytic cycle is the regeneration of $Co(dmpe)_2H$ from the product of eq 3, $Co(dmpe)_2{}^+$, as illustrated in Figure 1. The first step in this regeneration is the oxidative addition of H_2 to the cobalt(I) complex, $Co(dmpe)_2{}^+$, step B in Figure 1. The next step to complete the catalytic cycle is the deprotonation of the resulting cobalt(III)-dihydride ($Co(dmpe)_2(H)_2{}^+$) to regenerate the $Co(dmpe)_2H$, as illustrated in step C. The rapid deprotonation of $Co(dmpe)_2(H)_2{}^+$ requires a base that has a conjugate acid with a similar or higher pK_a value than $Co(dmpe)_2(H)_2{}^+$. Given the calculated pK_a value of 33.7 in acetonitrile for $Co(dmpe)_2(H)_2{}^+$,[21] Verkade's base (Vkd) is matched in energy, with a reported pK_a of 33.6 for its conjugate acid.[27]

Consistent with the above thermodynamic data,[28] we found $Co(dmpe)_2H$ is active for the hydrogenation of CO_2 to produce formate (Table 1, Figure 2). The production of formate was measured as a function of time using ^1H NMR spectroscopy for a tetrahydrofuran solution of $Co(dmpe)_2H$ and Verkade's base using a 1:1 mixture of CO_2:H_2 at 1.8 atm total pressure. The resulting rate of formate production was then converted to a catalytic turnover frequency (TOF, moles of formate per mole of cobalt per hour). A TOF of 850 h^{-1} was observed at a catalyst loading of 2.8 mM, as in the first entry in Table 1. The TOF increased as the catalyst concentration was decreased, suggesting that catalysis is mass-transport limited (occurring faster than the rate of gas−liquid mixing) at the higher concentration of catalyst.

Lowering the concentration of catalyst by an order of magnitude increased the observed TOF to 6400 h^{-1} at 1.8 atm. At only 1.0 atm of total pressure, a TOF of 3400 h^{-1} was obtained at the same concentration of catalyst. Using a similar catalyst concentration, the rate of CO_2 hydrogenation at 20 atm was too fast for our kinetic method, suggesting a TOF of ≥54 000 h^{-1}. At a lower catalyst concentration, the TOF increased and became consistent with an approximately first-order dependence on total pressure, as the TOF increased to 74 000 h^{-1} with an observed turnover number (TON) of 9400, entry 5.

Table 1. Catalytic Conversion of CO_2 and H_2 to Formate with $Co(dmpe)_2H$[a]

entry	catalyst loading[b] (mM)	base loading[b] (mM)	P (atm)	TOF (h^{-1})	TON
1	2.8	Vkd, 530	1.8	850	210
2	0.28	Vkd, 570	1.0	3400	2000
3	0.28	Vkd, 530	1.8	6400	1900
4	0.40	Vkd, 740	20	54000[c]	2100
5	0.040	Vkd, 510	20	74000	9400[d]
6	4.0	$P_1{}^tBu$, 710	20	830	190
7	40	DBU, 960	20	140	59
8	40	NEt_3, 1000	40	–	2
9	none	Vkd, 400	40	0	0

[a] Catalytic conditions; 350−500 μL of THF-d_8, 1:1 CO_2:H_2, 21 °C, all reactions went to completion within 60 min unless otherwise noted. [b] Initial concentration. Vkd = 2,8,9-triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane. DBU = 1,8-diazabicycloundec-7-ene. $P_1{}^tBu$ = *tert*-butylimino-tris(dimethylamino)phosphorane. NEt_3 = triethylamine. [c] Minimum TOF; reaction was complete before first NMR spectrum was collected at 2 min. [d] 65% complete.

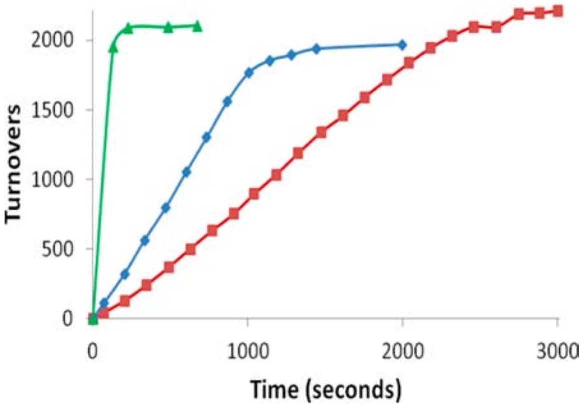

Figure 2. A plot of turnovers (mol formate/mol catalyst) vs time for $Co(dmpe)_2H$ at pressures of 1.0 (red squares), 1.8 (blue diamonds), and 20 atm (green triangles) of 1:1 CO_2:H_2 in THF-d_8 at 21 °C (Table 1, entries 2, 3, and 4, respectively).

To confirm that the strength of the base affects the TOF, we tested a range of weaker bases, specifically $P_1{}^tBu$ (a phosphazene base), DBU, and triethylamine, for which the corresponding conjugate acids have pK_a values of 28.4, 24.3, and 18.8, respectively.[29] The TOF decreased with decreasing basicity, 830 > 140 > 0 h^{-1}, respectively. Triethylamine is not sufficiently basic to deprotonate the $[Co(dmpe)_2(H)_2]^+$ to complete the catalytic cycle under the experimental conditions. With the weaker bases, substantial amounts of the cationic cobalt dihydride, $[Co(dmpe)_2(H)_2]^+$, were observed in the in situ ^1H and ^{31}P NMR spectra during the catalytic reactions, while only the neutral monohydride was observed during the catalytic reaction using Verkade's base. These observations support the premise that the deprotonation of the dihydride (step C in Figure 1) is rate-limiting when using milder bases but not with Verkade's base.

To demonstrate that the pK_a of the dihydride cation is as important as the hydricity, we investigated the rhodium analogue of our cobalt catalyst, Rh(dmpe)$_2$H, under identical conditions to those in entry 7 in Table 1. Under these conditions, a TOF of 17 h^{-1} was obtained, which is almost an order of magnitude slower than for Co(dmpe)$_2$H. Although the ΔG_{H^-} for Rh(dmpe)$_2$H is 23.6 kcal/mol, over 10 kcal better hydride donor than Co(dmpe)$_2$H (36.3 kcal/mol), the Rh(dmpe)$_2$(H)$_2^+$ is substantially less acidic with a pK_a of 36.7 compared to 33.7 for Co(dmpe)$_2$(H)$_2^+$. This decrease in acidity is consistent with lower catalytic performance, in spite of the improvement in the hydride donor ability.

Developing an understanding of how to rationally design complexes for the interconversion of energy and fuels is critical to the widespread utilization of carbon-neutral energy sources. By using thermodynamic parameters, we designed an active catalyst system for the hydrogenation of CO_2 using a known first-row transition metal complex. The catalytic activity of this first-row transition metal complex is comparable to the best precious metal catalysts for CO_2 hydrogenation, and this cobalt catalyst is active under milder conditions of temperature and pressure, as displayed in Table 1. For comparison, the present cobalt-based system is faster at room temperature than catalysts based on rhodium (1300 h^{-1} at 40 atm)[30] and similar to the fastest catalysts based on iridium (150 000 h^{-1} at 49 atm and 200 °C)[31] and ruthenium (95 000 h^{-1} at 200 atm and 50 °C).[32] In the present catalyst system, the use of an expensive and esoteric base may prevent scale-up or development into a commercially viable process; however, optimization of this system to use less specialized bases is underway. The present work demonstrates the utility of using fundamental thermodynamic parameters to help design an effective catalyst system: through matching the bond strength of the metal hydride to the corresponding value for formate, as well as matching the acidity of the metal-dihydride to the base, we were able to rationally construct a catalytic cycle for the hydrogenation of CO_2 using a complex of a first-row transition metal. Further mechanistic studies of this system and expansion of this method to other first row transition metal complexes is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, supporting NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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