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Metal Hydrides as Catalytic Intermediates: The Curious Case of Iron Carbonyl Clusters

Atefeh Taheri[1] and Louise A. Berben[2] Department of Chemistry, University of California, Davis, California 95616, United States

Abstract:

Here, we discuss recent efforts during the last 5 years for the development of molecular electrocatalysts involving metal hydride intermediates with particular attention to iron carbonyl clusters. This review begins with a brief description of thermodynamic properties (hydricity) of metal hydride intermediates and methods of hydricity measurements, specifically for iron carbonyl clusters. We then discuss two important reactions by iron carbonyl clusters relevant to solar fuel catalysis: electrocatalytic reduction of CO_2 to formate and proton reduction to hydrogen. These examples are included because they provide valuable mechanistic insights into the design of catalysts that produce hydrogenated products selectively from CO_2.

Keywords: Metal hydride, iron carbonyl cluster, CO_2 reduction, electrocatalyst, hydricity.

INTRODUCTION

Metal hydrides play a significant role in a broad range of chemical processes. Metal hydrides are perceived as key intermediates in various catalytic reactions such as proton reduction, H_2 oxidation and hydrogenation of CO_2 and CO.[1] The mechanisms of metal hydride bond formation and the interaction between the hydride and substrates are critical and can offer new research opportunities. There have been a few relatively recent prominent studies where various methods including electrochemical techniques are applied to probe the mechanism of formation and reaction of metal hydride intermediates in catalytic cycles.[2–6] In addition to mechanistic and kinetic studies on the formation of metal hydrides, there are various interesting literature reports, most significantly by DuBois and coworkers,[7–11] and by Creutz and coworkers,[12,13] that focus specifically on the thermodynamics of metal hydride reactivity.

The synthesis and characterization of iron carbonyl clusters have been well-studied for many years.[14–16] Iron carbonyl clusters containing interstitial anions such as nitride and carbide were first reported in the 1980's.[17,18] Recently these clusters have received much attention from our group as promising alternatives to noble metal electrocatalysts for H_2 gas production and CO_2 reduction in organic and aqueous solutions.[19–23] In a series of recent publications, we have described ability of the clusters with similar structures, $[Fe_4N(CO)_{12}]^-$, $[Fe_4C(CO)_{12}]^{2-}$, and $[Fe_4N(CO)_{11}(PPh_3)]^-$, to perform proton or CO_2 reduction.[21–23] These compounds are shown in chart 1. The nitride-bridged cluster (**1**$^-$) remains one of the most selective molecular catalysts for electrocatalytic CO_2 reduction to formate, with the best turnover number and frequency observed in neutral water. This compound is *the only* first row transition element electrocatalyst for selective formate production from CO_2.

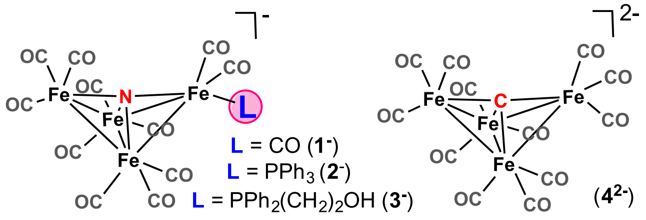

Chart 1. (Left) $[Fe_4N(CO)_{12}]^-$ (**1**$^-$), $[Fe_4N(CO)_{11}(PPh_3)]^-$ (**2**$^-$), and $[Fe_4N(CO)_{11}(PPh_2(CH_2)OH)]^-$ (**3**$^-$) and (Right) $[Fe_4C(CO)_{12}]^{2-}$ (**4**$^{2-}$).

Hydricity Definition and Measurement.

Hydricity is a thermodynamic property and is defined as the Gibbs free energy for loss of H^- as shown in equation 1:

$$\text{M-H (solv)} \longrightarrow \text{M}^+\text{ (solv)} + \text{H}^-\text{(solv)} \qquad \Delta G_{\text{H}^-} \qquad (1)$$

$\Delta G^o_{\text{H}^-}$ defines reaction driving forces and predicts the reactivity of a metal hydride. The reaction in equation 1 is defined independently of a specific hydride acceptor; however, it is strongly solvent-dependent. The determination of an absolute hydricity value is generally approached using various experimental methods based on thermochemical cycles developed mainly by DuBois and coworkers.[24] These measurements are primarily based on experiments performed in acetonitrile (MeCN) solution.

Aqueous hydride transfer is a primary step in emerging alternative energy transformations, which demonstrate a need for more thermochemical insights in aqueous solution. Very recently, several research groups including Yang's, Miller's and our group reported the hydricity values of metal hydrides in various solvents including water.[25,26] There are various methods used for hydricity measurements.[24] These measurements by our group were done using the thermodynamic cycles shown methods 1 (equations 2-6) and method 2 (equations 7-10). In equations 4 and 8, $\Delta G^{\circ}_{H_2}$ is the standard free energy for heterolytic H_2 cleavage showing the hydricity of H_2 in MeCN and water, respectively.[24,27] In MeCN, the equilibrium constant in equations 2 (K_{eq}) was determined by using organic acids with different strengths (K_{acid}) under 1 atmosphere of hydrogen gas (H_2). By carefully choosing a weak acid that reacts with reduced compound to produce hydride and does not react with metal hydride to produce H_2, the lower limit of K_{eq} was determined. Similarly, by choosing a strong acid that reacts with metal hydride and produces H_2 gas, an upper limit for the value of K_{eq} was determined.

Method 1. *Hydricity measurement in MeCN.*

$$[\text{H-M}]^{n} + \text{HA} \rightleftharpoons [\text{M}]^{n+1} + \text{H}_2 + \text{A}^{-} \qquad K_{eq} \qquad (2)$$

$$\text{H}^{+} + \text{A}^{-} \rightleftharpoons \text{HA} \qquad 1/K_{acid} \qquad (3)$$

$$\text{H}_2 \rightleftharpoons \text{H}^{+} + \text{H}^{-} \qquad \Delta G^{\circ}_{H_2} \qquad (4)$$

$$[\text{H-M}]^{n} \rightleftharpoons [\text{M}]^{n+1} + \text{H}^{-} \qquad \Delta G^{\circ}_{H-} \qquad (5)$$

$$\begin{aligned}\Delta G^{\circ}_{H-} &= \Delta G^{\circ}(\text{eq } 2) + \Delta G^{\circ}(\text{eq } 3) + \Delta G^{\circ}_{H_2}\\ &= 1.37\ \text{p}K_{eq} - 1.37\ \text{p}K_{acid} + 76\ \text{kcalmol}^{-1} \qquad (6)\end{aligned}$$

Alternatively, equations 7-10 were used to determine the hydricity values in aqueous conditions. In solutions with low pH, metal hydride reacted with proton to produce hydrogen gas in solutions with higher pH, lower concentration of proton, the equilibrium shown in equation 7 is directed to the left. By cautiously changing the pH of solutions, the low and high limits for these two conditions were determined. The results are summarized in Table 1.

Method 2. *Hydricity measurement in H_2O.*

$$[\text{H-M}]^{n} + \text{H}^{+} \rightleftharpoons [\text{M}]^{n+1} + \text{H}_2 \qquad K_{eq} \qquad (7)$$

$$\text{H}_2 \rightleftharpoons \text{H}^{+} + \text{H}^{-} \qquad \Delta G^{\circ}_{H_2} \qquad (8)$$

$$[\text{H-M}]^{n} \rightleftharpoons [\text{M}]^{n+1} + \text{H}^{-} \qquad \Delta G^{\circ}_{H-} \qquad (9)$$

$$\begin{aligned}\Delta G^{\circ}_{H-} &= \Delta G^{\circ}(\text{eq } 7) + \Delta G^{\circ}_{H_2}\\ &= 1.37\ \text{p}K_{eq} + 34.2\ \text{kcalmol}^{-1} \qquad (10)\end{aligned}$$

Table 1. Hydricity of metal carbonyl hydride intermediates, H_2 and formate in MeCN and H_2O.

Compound	ΔG°_{H-} (kcal mol^{-1})	
	MeCN	H_2O
$[HFe_4C(CO)_{12}]^{2-}$	44[22]	< 15[22]
$[HFe_4N(CO)_{12}]^{-}$	49[21]	15.5[21]
$[HFe_4N(CO)_{11}(PPh_3)]^{-}$	45-46[23]	ND
H_2	76[24]	34.2[27]
$HCOO^{-}$	44[28]	24.1[27]

ND: Not Determined

The driving force of hydride transfer, $\Delta(\Delta G^{\circ}_{H-})$, from metal hydride to protons or CO_2 is calculated based on the difference in hydricity between metal hydride and formate ($HCOO^{-}$) or hydrogen molecule (H_2), respectively. The results are displayed in Table 2. The hydricity of metal hydrides is especially important for their reaction with CO_2, which is usually accompanied by unwanted H_2 gas production.

Table 2. Free energy of hydride transfer $\Delta(\Delta G^{\circ}_{H-})$ from metal carbonyl hydride intermediates to H^{+} and CO_2 to produce H_2 and formate in MeCN and H_2O.

Compound	$\Delta(\Delta G^{\circ}_{H-})$(kcal mol^{-1})			
	H^{+}		CO_2	
	MeCN	H_2O	MeCN	H_2O
$[HFe_4C(CO)_{12}]^{2-}$	-32	<-34.2	0	<-8.6
$[HFe_4N(CO)_{12}]^{-}$	-27	-18.7	5	-8.6
$[HFe_4N(CO)_{11}(PPh_3)]^{-}$	-(30-31)	ND	1-2	ND

Metal Hydride Intermediates in Electrocatalytic H_2 and Formate Production.

The iron carbonyl clusters in the electrocatalytic reactions have been studied in MeCN,[19] water/ MeCN mixtures, and in aqueous solution.[21] It was observed that in MeCN $\mathbf{1}^-$ produced H_2 as the sole product when a strong acid (e.g. *p*-toluenesulfonic acid) was the proton source, but some formate was detected in the presence of weaker acids (e.g. benzoic acid). A high selectivity for formate with 95% Faradaic efficiency was observed in both a 95:5 MeCN: H_2O solvent mixture and aqueous buffer solutions (pH 5-13).

Various electrochemical and spectroscopy methods were used to study the catalytic intermediates and the thermochemical properties of the catalysts. Cyclic voltammetry experiments provided the evidence for the formation a metal hydride intermediate, $[HFe_4N(CO)_{12}]^-$, when electrochemically reducing $[Fe_4N(CO)_{12}]^-$ in the presence of proton sources. Furthermore, it was shown that $[HFe_4N(CO)_{12}]^-$ reacted with CO_2.[21] Infra-red spectro-electrochemistry (IR-SEC) experiments showed the additional spectroscopy evidence for formation of $[HFe_4N(CO)_{12}]^-$ and enabled the measurement of the equilibrium constant for determining the acidity and hydricity of this metal hydride intermediate in both water and acetonitrile. Using IR-SEC method, it was observed that in the absence of CO_2 in pH 5-12 aqueous buffered solutions, this intermediate reacts quantitatively with H^+ to afford H_2. At pH 13, with very low concentration of protons, the iron hydride intermediate persisted in solution and was detected by IR spectroscopy.

The crystal structure of $[HFe_4N(CO)_{12}]^-$ was obtained and confirmed the formation of this hydride intermediate. It was observed that the hydride bridged two iron centers along the butterfly wing. The significance of this observation is discussed in the next section. The chemical reaction of CO_2 and this hydride resulted in the formation of $HCOO^-$, which is a strong evidence for the importance of this metal hydride intermediate in the catalytic production of $HCOO^-$.

The free energy for C-H bond formation by reaction of $[HFe_4N(CO)_{12}]^-$ with CO_2 is thermodynamically unfavorable in MeCN but favorable in water by 5 and 8.6 $kcalmol^{-1}$, respectively (table 2). This is consistent with our experimental results where we observed an improved selectivity for formate production on moving from pure MeCN, to 95:5 MeCN: H_2O, to aqueous systems. The hydricity of formate in the 95:5 MeCN: H_2O solvent mixture has not been measured. However, at the formic acid acidity gets closer to water value in MeCN: H_2O solvent mixture, it is expected that the hydricity of formate to shift closer to the values in water as well.[1]

It was observed that the carbide-containing cluster with a very similar structure, $\mathbf{4}^{2-}$ (chart 1), produced H_2 gas as the sole product even in the presence of CO_2 in MeCN, 95:5 MeCN: H_2O, and buffered aqueous solutions (pH 5 - 12).[22] The experimental hydricity measurements predict that in acetonitrile the hydride transfer from the proposed intermediate $[HFe_4C(CO)_{12}]^{2-}$ to CO_2 is thermoneutral, and to H^+ is thermodynamically favorable (table 2). In water, the hydride transfer to both H^+ and CO_2 is thermodynamically favorable (table 2). These results suggest that perhaps, the lower hydricity of $[HFe_4N(CO)_{12}]^-$ compared to that of $[HFe_4C(CO)_{12}]^{2-}$ provides the needed selectivity to obtain formate.

More recently, our group looked at the use of proton relays to alter the outcome of an electrocatalytic reaction.[23] Two phosphine-substituted clusters were synthesized: hydroxyl-containing $[Fe_4N(CO)_{11}(PPh_2EtOH)]^-$ ($\mathbf{3}^-$), and $[Fe_4N(CO)_{11}(PPh_3)]^-$ ($\mathbf{2}^-$) which was used for comparison. In 95:5 MeCN: H_2O solution, CO_2 reduction to formate is catalyzed by $\mathbf{2}^-$. In contrast, the hydroxyl containing cluster produced only H_2 under catalytic conditions. In this system the hydroxyl group functions as a proton shuttle.

Bridging Hydrides as Intermediates.

Numerous studies have reported the thermodynamics and kinetics of hydride transfer and interactions of metal hydrides with various organic substrates.[1] However, the vast majority of studies have examined monometallic complexes with terminal hydrides. Bridging hydrides usually appear as byproducts from unwanted side reactions. For example, Stasunik and Malisch observed the formation of $[Cp^*(CO)_2Ru]_2(\mu\text{-}H)\}^+$ by protonation of the neutral dimer $[Cp^*(CO)_2Ru]_2$.[29] In another study, Heinekey and co-workers observed the same hydride-bridged compound from the decomposition of the reactive dihydrogen complex $[Cp^*(CO)_2Ru(\eta^2\text{-}H_2)]^+$.[30] Bullock and Cheng found that $[Cp^*(CO)_2Os]_2(\mu\text{-}H)\}$ was produced from an analogous reaction with osmium hydride.[31] Bridging hydrides are generally less reactive than their terminal counterparts. For example, the mononuclear species, $[HM(CO)_5]_2^-$ (M = Cr, Mo, and W), reacts with acids much more readily than bridging hydride forms $\mu\text{-}H[M(CO)_5]_2^-$.[32,33] Later studies by DuBois and workers confirmed that these terminal hydride tungsten complexes are very powerful hydride donors.[34] In addition, Darensbourg and coworkers observed that while $[HM(CO)_4(L)]_2^-$ (L= PPh_3, PMe_3, $P(OMe)_3$) reacts with alkyl halides to yield alkanes, their corresponding bridging hydrides do not.[35–37]

The low reactivity of bridging hydrides might be a valued characteristic in addressing one of the biggest challenges in the development of the catalyst for CO_2 reduction – product selectivity. Hydrogen gas is often the main undesired side product during CO_2 reduction. Unlike what was thought in the past, choosing the most hydridic catalyst does not ensure selective conversion of CO_2 to formate. It now seems that the better approach is to design the catalyst and conditions that are just hydridic enough to react with CO_2 while minimizing the rate of hydrogen evolution.[38] The weaker reactivity of bridging hydrides makes them potentially the perfect match for this strategy.

Future Directions.

Future work focuses on the detailed analysis of the kinetics of metal hydride formation and the follow-up reactions of metal hydrides with substrates. Particularly, the focus will be on the reaction between electrochemically formed metal hydrides and CO_2. Various research groups have done extensive systematic analysis of complicated electrochemical data in order to understand the mechanism of many electrocatalytic reactions,[39] specifically for oxygen reduction and hydrogen evolution electrocatalysts;[40–42] however similar studies for CO_2 reduction is rare. Our future work will focus on understanding the mechanism of CO_2 reduction by molecular electrocatalysts and design of new catalysts with improved rates for reaction with CO_2.

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