Electrohydrogenation: Enabling Science for Renewable Fuels

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Abstract
A series of molecular complexes have been prepared and shown to activate and/or reduce carbon dioxide, ketones, and protons. These advances illustrate the potential of highly reactive transfer hydrogenation catalysts to act as catalyst precursors for the reduction of CO₂ and other biomass-derived feedstocks to energy dense liquid fuels. We have tested several well-defined molecular complexes designed to activate and reduce carbon-dioxide, ketones and protons. These studies have helped illuminate the electronic and structural features of coordination complexes whose metal and coordinated ligands can function cooperatively to facilitate reactivity with protons, electrons, and carbonyl compounds such as ketones, and carbon dioxide. We have also developed new classes of ketone reduction catalysts based on earth-abundant Mo and Co complexes.

Introduction
The goal of this project is to develop energy-efficient catalysts for electrohydrogenation reactions to create and upgrade liquid fuels. The ultimate goal is to develop efficient strategies for the use of renewable sources of electricity to produce liquid fuels from CO₂ and to upgrade biomass to energy-dense liquid fuels.

Aim 1: To apply concepts from transfer hydrogenation to develop new catalysts for the energy efficient and rapid activation and reduction of CO₂, ketones and carbonyl containing molecules derived from biomass.

Aim 2: To apply concepts of proton-coupled electron transfer as a strategy for the electrochemical generation of metal hydrides.

Aim 3: To develop energy efficient catalysts for the electrocatalytic reduction of CO₂ and other C=O containing molecules.

Background
A sustainable energy economy will require the use of renewable sources as principal energy inputs. The energy-efficient conversion of electricity to chemical fuels is a critical component of a future energy economy, as intermittent renewable energy cannot be widely utilized unless it can be captured and stored. The storage of intermittent electricity, either by reduction of CO₂ to liquid fuels or by up-grading biomass, are grand challenges: few efficient electrohydrogenation catalysts exist.[1,2] The reduction of CO₂, either by chemical hydrogenation or electroreduction, is a formidable challenge[3] as CO₂ is both kinetically and thermodynamically inert and the products of CO₂ partial reduction, formic acid and formates, are likewise resistant to reduction.[4] Our ultimate
objective is to develop new families of electrocatalysts for the electrohydrogenation of CO$_2$ to energy-rich liquid fuels, such as methanol. The direct electrohydrogenation of CO$_2$ would provide a strategy for the conversion of renewable electrical energy to liquid fuels.

Our objective is to develop new approaches to CO$_2$ activation and electrochemical hydrogenation at low overpotential. While both energy efficiency ("overpotential" and Faradaic efficiency) and current density (rate) are critical for large-scale implementation, it is our view that the gaps in our understanding of the energetic requirements of critical chemical steps for reversible electrohydrogenation are the major impediments to further progress.

The innovation of our approach is based on the hypothesis that catalysts that mediate transfer hydrogenation of ketones (Fig 1) are promising candidates as catalysts for electrocatalytic hydrogenation for both thermodynamic and kinetic reasons. Thermodynamically, the reversible potential for hydrogenation of CO$_2$ to methanol (-0.031 V vs. RHE, 25°C) is similar to that for the reversible potential of acetone hydrogenation to isopropanol (0.12 V vs. RHE, 25°C). That the M-H intermediates are generated rapidly from isopropanol in transfer hydrogenation reactions means that these hydrides are formed readily and reversibly at potentials that correspond to the thermodynamic potential for ketone hydrogenation. This provides a compelling argument that the formation of these M-H complexes is thermodynamically feasible at potentials close to that for the hydrogenation of C=O bonds of ketones, formates and CO$_2$.

The bi-functional mechanisms (Fig 1) proposed for certain classes of ketone transfer hydrogenation catalysts provide a promising strategy for lowering the kinetic barriers for CO$_2$ activation and reduction. One of the key principles derived from studies of homogeneous transfer hydrogenation is the concept of dual-site cooperativity, whereby a redox-active transition metal such as Ru, Fe, or Ni is in close proximity to heteroatoms, such as O, N, or S such that a hydride and a proton are delivered to the C=O bond in one step to effect the overall hydrogenation (Fig. 1).[5,6]

Several recent studies have shown that homogeneous molecular catalysts can utilize hydrogen to reduce CO$_2$ or esters;[4,7] what distinguishes our approach is our strategy for translating this promising chemical reactivity into efficient electrohydrogenation reactivity.
Results Sept. 1, 2014 - May 1, 2015.

New catalysts and new reactivity: Our synthetic efforts have focused on two areas: 1) to explore the reductive chemistry of highly active transfer hydrogenation catalysts, and 2) to design new complexes for reduction of CO₂, carbonyl containing compounds and/or protons.

Kinetics and Thermodynamics of Ru-H reactions with ketoness and CO₂. We have continued our investigations into the chemical and electrochemical reactivity of the highly active transfer hydrogenation catalyst ruthenium hydride [HRu(CNN)(dppb)] (CNN = 6-(4'-methylphenyl)-2-pyridylmethylamine, dppb = Ph₂P(CH₂)₄PPh₂). In the last grant period, we have taken advantage of the expertise of our colleague Todd Martinez to expand our theoretical efforts utilizing the recently developed TeraChem quantum chemistry software. These studies have enabled us to use theoretical simulations to benchmark theoretical calculations against experimental measurements for both the reversible reduction of acetone by the Ru-H and the rapid reduction of CO₂ to the Ru formate (Figure 2).

![Diagram of Ru-H insertion reactions](image)

**Figure 2:** (a) Thermodynamics of Ru-H insertion reactions, (b) Calculated transition-state for CO₂ insertion

The Ru-H 1 reacts rapidly upon mixing with CO₂, affording the Ru formate complex 3, but the formate 3 does not liberate CO₂ to regenerate the hydride, even upon extended thermolysis in solution. Thus, while the rapid rate of CO₂ activation is attractive, the insertion of CO₂ to generate the formate 3 is likely to be too exergonic (ΔG₀ = -11.3 kcal mol) for a reversible reduction of CO₂ in an electrocatalytic cycle.

We employed DFT calculations to illuminate the origin of the rapid activation of CO₂ as well as to predict the optimal ligand environment for reversible insertion reactions. These calculations indicate that the facile activation of CO₂ is a consequence of a cooperative effect between the Ru-H and the N-H of the coordinated amine ligand. In addition, these calculations predict that introducing an amine ligand trans to the reactive X group (Figure 3, X = H, OR, OCHO, complex 4), would result in reactive intermediates whose free energies are closer in energy. These calculations predict that the Ru-H derived from 4 would be expected to undergo both rapid and reversible insertions of both acetone and CO₂ (Figure 3).
These calculations have stimulated renewed efforts to generate complex 4 to test these predictions and to generate more rapid and reversible CO$_2$ reduction catalysts.

New classes of Earth abundant complexes for transfer hydrogenation and electroreduction: As part of our efforts to develop catalysts based on earth-abundant metals for transfer hydrogenation reactions and electrohydrogenation catalysts, we have generated a family of Mo and Co complexes ligated by redox- and proton-active ligands. Our hypothesis is that redox-active ligands will be able to store charge at similar potentials, facilitating multi-electron (and proton) transfers. To this end, we have prepared a new class of Mo complexes bearing cyclopentadienone ligands[10] and have shown these to be competent transfer hydrogenation catalysts for the reduction of cyclohexanone by isopropanol (Figure 4a). This is the first example of a catalytically-active Mo analog of the well known Ru Shvo transfer hydrogenation catalyst.[11,12] We have also generated novel examples of Co cyclopentadienone complexes and hydroxycyclopentadienyl complexes of Cobalt (Figure 4b).
We have also prepared the related cyclopentadienyl Co complexes 7 and 8 bearing the proton-active pyridylpyrazole ligand and the redox-active phenyl azo-pyridyl ligand (Figure 5). Both complexes are active electrocatalysts for the reduction of protons to H₂, albeit at rather negative potentials.

Figure 5: Cyclopentadienyl Co complexes bearing proton- and redox-active ligands.

Cyclic voltammetry of complex 8 reveals that the Co(III) complex is reduced reversibly by two electrons at very modest potentials (-0.16 V vs. Fc⁺/Fc) in acetonitrile to afford the Co(I) complex 9 (Figure 6). Moreover reduction of 8 in acid generates the hydrazido complex 10. Independent measurements reveal the pKa of 10 to be approx. 14.3; these measurements indicate that the hydrazido complex 10 is a competent hydrogen atom donor as the bond-dissociation free energy of the N-H bond in 10 is calculated to be approximately 62-65 kcal/mol. This value is supported by preliminary experiments which reveal that 10 can donate a hydrogen atom to the stable radical TEMPO (BDFE = 67 kcal/mol). These results reveal the rich reaction chemistry of proton- and redox-active ligands and are providing new conceptual approaches to electrochemically regenerable hydrogen atom donors.

Figure 6: Reversible Proton and Electron Transfers for Compound 8

New classes of Re and Mn complexes for selective electroreduction of CO₂. We have prepared a new class of Re and Mn carbonyl complexes to investigate the selective reduction of CO₂ to CO. The Re(I) and Mn(I) carbonyl complexes (N-N)MCl(CO)₃ have been widely investigated as electrocatalysts,[13-17] these complexes exhibit the unusual property of mediating the selective reduction of CO₂ to CO in the presence of protons.[17] The selective reduction of CO₂ rather than protons is a unique feature of
these complexes which has been attributed to a ligand-based reduction to generate reduced complexes with a delocalized electronic structure that selectivity binds CO$_2$ rather than protons (Figure 7).[17]

We have shown that the replacement of bipyridine ligands with the redox-active azopyridine ligands leads to active catalysts for CO$_2$ reduction. Moreover the reduction of the azopyridine complexes occurs at more positive potentials than that of the corresponding bipyridine complexes. For example, the rapid two-electron reduction of the (azopyridine)Mn(I)(CO)$_3$Br occurs at -0.9 V vs. ferrocene, 600 mV more positive than the corresponding reduction of the corresponding bipyridyl complex (mesbpy)Mn(I)(CO)$_3$Br.[16] These results are promising leads for the generation of CO$_2$ reduction catalysts that can operate at lower overpotential.

![Figure 7: Electrocatalytic CO$_2$ reduction with Re(I) carbonyl complexes; [17] electrochemical reduction of (azopyridine)Mn(I) complexes.](image)

**Figure 7:** Electrocatalytic CO$_2$ reduction with Re(I) carbonyl complexes; [17] electrochemical reduction of (azopyridine)Mn(I) complexes.

**Progress**

In the third year of this project, we have developed a new class of Co electrocatalysts for proton reduction and have developed a new series of homogeneous transfer hydrogenation catalysts derived from earth-abundant Mo and Co complexes. We have also developed a new class of CO$_2$ reduction catalysts based on Re and Mn complexes ligated by redox-active azopyridine ligands. Should our ongoing efforts to develop efficient electrohydrogenation catalysts for the reduction of CO$_2$ to methanol prove successful, this research will provide a strategy for the more widespread use of renewable and/or intermittent energy sources, such as wind, hydroelectric and solar energy.

**Future Plans**

A key objective of our ongoing efforts is to develop catalytic strategies for CO$_2$ reduction based on the promising reactivity of the Ru-H complexes 1. We plan to investigate the electrocatalytic behavior of the Mo and Co complexes in order to evaluate the potential of redox- and proton-active ligands to facilitate key proton and electron transfer steps necessary for multi-electron electrohydrogenation reactions. Theoretical
studies will play an increasing important role, as preliminary investigations are providing key insights on the influence of stereoelectronic ligand effects on the thermodynamics of metal hydrides. The promising electrocatalytic reduction chemistry of the cobalt, rhenium and manganese complexes are providing promising leads to new catalysts for the electrocatalytic reduction of carbon dioxide.

**Publications and Patents**


**References**


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