

Electrohydrogenation: Enabling Science for Renewable Fuels

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Abstract

A series of molecular metal hydrides derived from transfer hydrogenation catalysts have been shown to activate and/or reduce methyl formate, carbon dioxide 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, alkyl formates 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, formates and C=O 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 electrohydrogenation 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 CO₂ to energy-rich liquid fuels, such as methanol. The direct electrohydrogenation of CO₂ would provide a strategy for the conversion of renewable electrical energy to liquid fuels.

Our objective is to develop new approaches to CO₂ 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 CO₂ 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 CO₂.

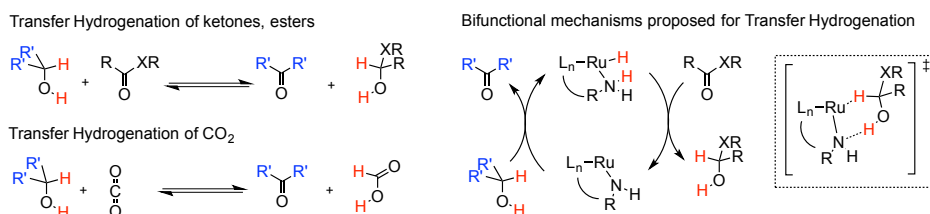


Figure 1: Transfer Hydrogenation of Ketones, Esters and CO₂.

The bifunctional mechanisms (Fig 1) proposed for certain classes of ketone transfer hydrogenation catalysts provide a promising strategy for lowering the kinetic barriers for CO₂ 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 CO₂ or esters;[4,7] what distinguishes our approach is our strategy for translating this promising chemical reactivity into efficient electrohydrogenation reactivity.

Results May 1, 2013 - April 30, 2014.

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

Kinetics and Thermodynamics of Ru-H reactions with carbonyl compounds, 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).^[8] We have experimentally determined the free energies for the insertion reaction of various carbonyl compounds (ketones, CO₂) into this ruthenium hydride, and used these results to calibrate our DFT models for this system (Figure 2). Insertion of ketones into the Ru-H is calculated to be exergonic by -2.9 kcal/mol, consistent with equilibrium measurements that indicate that these reactions are not strongly exergonic. In contrast, preliminary calculations on the insertion of CO₂ into the Ru-H indicates that this reaction is exergonic by approx. 5-7 kcal/mol, consistent with experimental observations that the resulting Ru formate does not readily eliminate CO₂ to regenerate the Ru-H **1**. DFT calculations indicate that the addition of ketones or CO₂ is facilitated by the cooperative addition of both a hydride and proton mediated by the Ru-H and N-H bonds of the hydride **1** (Figure 2, right).

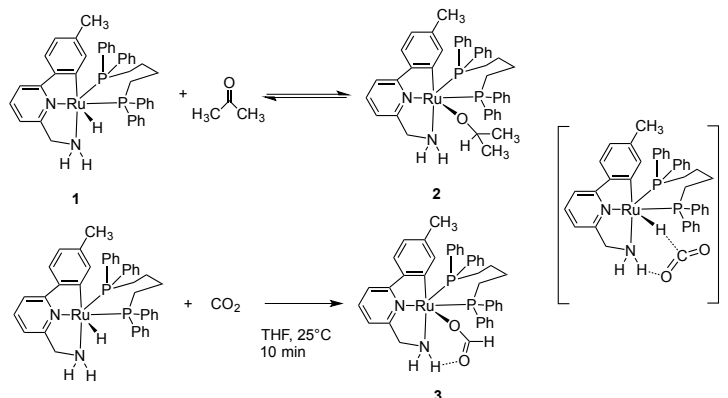


Figure 2: Kinetics and Thermodynamics of Ru-H insertion reactions

Stoichiometric and Catalytic reduction of CO₂. The Ru formate complex **3** reacts with sodium isopropoxide to liberate formate and the Ru-isopropoxide **2** which subsequently eliminates acetone and generates the Ru-H **1** (Figure 3).

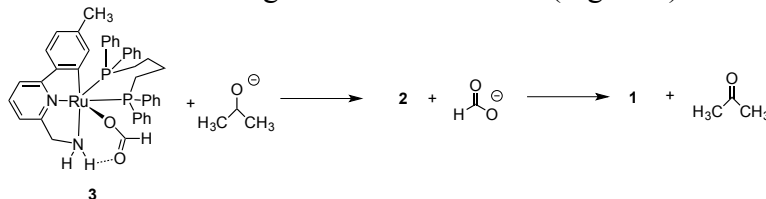


Figure 3: Reaction of Ru Formate to generate Formate

This reactivity provides a sequence of reactions that could generate a catalytic cycle for the reduction of CO₂ with isopropoxide. Preliminary experiments reveal catalytic reactivity for the reduction of CO₂ with isopropoxide in the presence of a catalytic amount of the Ru-H **1**, but further studies are required to confirm these results.

New classes of Earth abundant complexes for transfer hydrogenation and electroreduction: We have extended our studies of the Ru transfer hydrogenation catalyst **1** to other classes of transition metal complexes that are ligated by proton- and redox-active ligands. The Ru complex **4**, known as Shvo's catalyst,[9] is an active transfer hydrogenation catalyst that is proposed to reduce ketones by a cooperative hydride and proton-transfer mechanism (Figure 4). The dimeric hydride **4** dissociates at elevated temperature to generate a Ru(II) hydride **5** bearing a hydroxycyclopentadienyl ligand and a Ru(0) complex ligated by a cyclopentadienone ligand. In the reduction of ketones, both the hydroxycyclopentadiene ligand and the Ru center are redox active, indicating that both the ligand and metal function cooperatively.

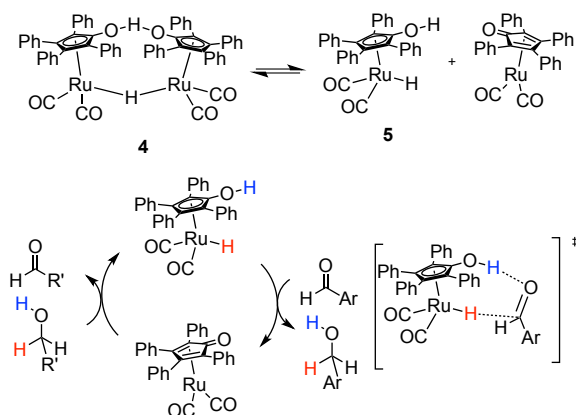


Figure 4: Shvo catalyst, bearing a proton- and redox-active cyclopentadienone ligand.

We have prepared the monomeric Ru-H **6** [9](Figure 5) and investigated its electrochemistry to assess if these complexes might function as electrocatalysts for CO₂ reduction.

We have also prepared related complexes based on more earth-abundant metals, such as the Mo complex **7**[10] and the novel Co complex **8**. The Mo complex **7** was recently discovered to be an active catalyst precursor for the transfer hydrogenation of ketones with isopropanol; the electrochemistry of this complex is currently being investigated to assess if it could act as a electrohydrogenation catalyst.

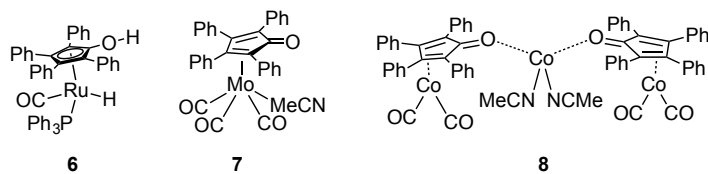


Figure 5: Ru, Mo and Co complexes bearing cyclopentadienone ligands.

We have also prepared the related cyclopentadienyl Co complexes **9** and **10** bearing the proton-active pyridylpyrazole ligand (complex **9**) and the redox-active phenyl azopyridyl ligand (complex **10**). Both complexes are active electrocatalysts for the reduction of protons to H₂ (Figure 7), albeit at rather negative potentials.

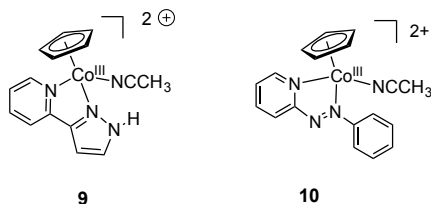


Figure 6: Cyclopentadienyl Co complexes bearing proton- and redox-active ligands.

Cyclic voltammetry of complex **10** reveals that the Co(III) precursor is reduced by two electrons at -0.16 V (vs. Fc⁺/Fc) in acetonitrile. Preliminary evidence suggests that both the Co center and the ligand are each reduced by one electron. Nevertheless, the onset of electrocatalytic current for the reduction of protons occurs at more negative potentials (-1.3 V vs. Fc⁺/Fc), but more positive of that of the Co(II)/Co(I) redox potential.[11,12] These preliminary results are promising, but require further investigations to illuminate the steps responsible for the key electron and proton transfer reactions.

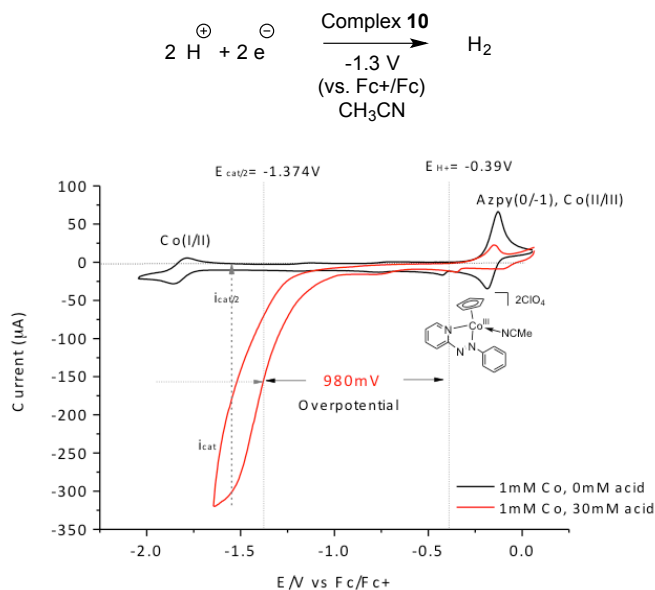


Figure 7: Electrocatalytic proton reduction with Co complex **10**.

Progress

In the second 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. Should our ongoing efforts to develop efficient electrohydrogenation catalysts for the reduction of CO₂ 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

In the next year, a key objective will be to develop catalytic strategies for CO₂ 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 complexes will be extended to the more challenging electrocatalytic reduction of ketones, esters and carbon dioxide.

Publications and Patents

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