UC Irvine
UC Irvine Previously Published Works

Title
For CO2 Reduction, Hydrogen-Bond Donors Do the Trick

Permalink
https://escholarship.org/uc/item/4vz9540h

Journal
ACS Central Science, 4(3)

ISSN
2374-7943

Authors
Chabolla, Steven A
Yang, Jenny Y

Publication Date
2018-03-28

DOI
10.1021/acscentsci.8b00087

Peer reviewed

For CO$_2$ Reduction, Hydrogen-Bond Donors Do the Trick

Steven A. Chabolla and Jenny Y. Yang

Department of Chemistry, University of California, Irvine, California, 92697, United States

Theory and experiment join forces to provide a comprehensive view on how pendant amines in the secondary coordination sphere impact electrocatalytic CO$_2$ reduction.

Carbon dioxide is the major pollutant responsible for climate change, an unfortunate byproduct of powering our society with fossil fuels. There is currently great interest in applying renewable energy to capture and reduce CO$_2$ to provide carbon-neutral fuels. This approach mimics natural photosynthesis, which utilizes CO$_2$ for energy storage and as a structural building block. Achieving this goal requires catalysts that can reduce CO$_2$ to higher energy products or fuel precursors. A popular target reaction is the two-electron reduction of CO$_2$ to CO. Along with H$_2$, CO can be used in Fischer–Tropsch processes to generate liquid fuels. In this issue of *ACS Central Science*, Chapovetsky, Welborn, and co-workers describe an integrated experimental and computational investigation into mechanistic pathways for a series of cobalt complexes that catalyze this reaction.[1] The most active catalyst contains architectural features that are known to facilitate CO$_2$ reduction in other molecular catalysts. However, their detailed analysis contained some surprises — and illuminates new ways in which the secondary structure can be harnessed to promote high catalytic activity.

The initial cobalt catalyst reported by Chapovetsky and co-workers contains four secondary amines along the ligand backbone (**1** in Figure 1).[2] The pendant N–H groups appear to be poised to assist CO$_2$ binding through hydrogen-bonding interactions; this binding motif has been observed in a structurally similar Ni(cyclam)$^{2+}$ catalyst.[3] The N–H assist hypothesis was buoyed by the strong positive dependence on the number of groups and catalytic rate. However, the calculated energies for CO$_2$ binding in this fashion contained an unexpected result: the ring flip required to position the N–H for CO$_2$ binding came at a prohibitively high energetic cost, and is inaccessible under catalytic conditions. Instead, the reason analogues with sequentially
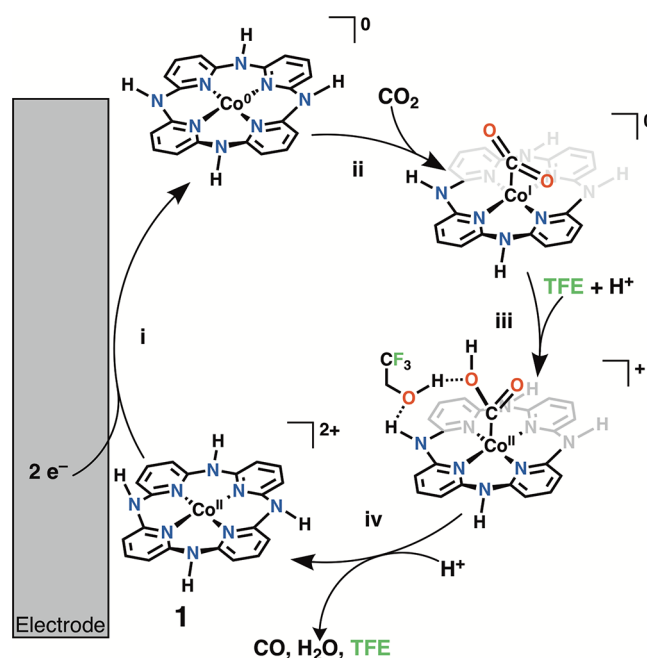

Figure 1. Adapted from the catalytic cycle proposed by Chapovetsky et al. for the hydrogen-bond assisted reduction of CO$_2$.[2] The Co(II) catalyst is reduced at the electrode (i), followed by formation of a CO$_2$ preassociation complex (ii) and rapid initial protonation (iii). The rate-determining second protonation step is facilitated by a hydrogen-bonding interaction with the TFE acid (iv) to yield CO and H$_2$O.

methylated amines (pendant R$_2$N–H groups replaced by R$_2$N–CH$_3$) have lower catalytic activity is their increased steric profile, which inhibits CO$_2$ binding.

> However, the calculated energies for CO$_2$ binding in this fashion contained an unexpected result: the ring flip required to position the N–H for CO$_2$ binding came at a prohibitively high energetic cost, and is inaccessible under catalytic conditions.

The presence of proximal hydrogen-bond donors is also known to assist CO$_2$ reduction by mediating proton movement.

(For a prominent example, see phenol modified Fe(porphyrin), Costentin et al.)[4] However, the computational results again indicate that direct protonation from the N−H group would require an energetically challenging conformational change. Instead, the N−H groups play a role in orienting the acid for the rate-determining second protonation step (Figure 1, step iv).

The detailed analysis of the catalytic cycle results in a rate law that quantifies the contribution of installing each N−H group in the ligand backbone on overall activity. Achieving this thorough understanding of the relationship between structure and function would likely have been impossible without the cooperative use of experimental observations and theoretical calculations. Ultimately, the unexpected role the N−H groups play in the catalytic cycle underscore the importance of considering structural dynamics in secondary coordination sphere interactions.[5]

The most active variant, **1**, with four pendant N−H groups, is both fast and selective for the product CO, with few electron equivalents going toward side reactions (such as direct proton reduction to H_2). However, it operates with a high overpotential (η), a reflection of energetic inefficiency. With these properties, it joins an exclusive group of CO_2 reduction catalysts that score high on key reactive metrics (selectivity and activity), but require improvement in others (η). A collective examination of mechanistic studies for molecular CO_2 reduction catalysts may not appear to coalesce around any single structural feature or challenging catalytic step that would provide cohesive guidelines for catalyst design. This complexity is a consequence of the multivariable challenges associated with optimizing this reaction. Many catalysts rely on highly reducing metal centers to activate relatively inert CO_2, but at the price of high overpotential. In other cases, the release of the product CO, a good ligand for electron rich metal centers, limits the catalytic rate. Achieving high product selectivity also requires inhibiting proton reduction pathways. Additionally, as in most multi-electron and -proton reactions, uncoupled movement of the latter can contribute to sluggish kinetics or high energy barriers in the catalytic cycle.[6] Studies on catalysts that have overcome these challenges reveal insight into circumventing these troublesome catalytic steps. In Ni(cyclam)$^{2+}$ and the phenol-modified Fe(porphyrin) catalysts mentioned previously, cooperative CO_2 binding through hydrogen-bonding interactions enables catalysis at milder potentials while also serving as proton shuttles. Additionally, insight into the electronic structure of reduced metal centers provides valuable information on how to inhibit competitive proton reduction pathways and ease CO release.[7] Many other

strategies to improve catalyst performance, including incorporation of electrostatic interactions, are also emerging.[8] Can all of these considerations be pieced together to achieve an optimal catalyst?

> A collective examination of mechanistic studies for molecular CO_2 reduction catalysts may not appear to coalesce around any single structural feature or challenging catalytic step that would provide cohesive guidelines for catalyst design.

Many of the aforementioned considerations are actually already assembled in a single − albeit non-synthetic − catalyst. Electrochemical studies on the enzyme *Ch* CODH I from the anaerobic thermophile *Carboxydothermus hydrogenoformans* indicate fast and reversible interconversion of CO_2 and CO with almost no overpotential indicating near-perfect energy efficiency.[9] Structural studies on the active site point to many of the elements described above, including cooperative CO_2 binding and utilizing the local microenvironment to mediate proton movement.[10] Investigating the importance and impact of these interactions using both experiment and theory is crucial to achieving a synthetic catalyst with high rates, selectivity, and thermodynamic efficiency. In this way, we have the potential to mimic nature and master the art of CO_2 chemistry.

Author Information
E-mail: j.yang@uci.edu.
ORCID
Jenny Y. Yang: 0000-0002-9680-8260

REFERENCES

(1) Chapovetsky, A.; Welborn, M.; Luna, J.; Haiges, R.; Miller, T.; Marinescu, S. Pendant hydrogen-bond donors in cobalt catalysts independently enhance CO_2 reduction. *ACS Cent. Sci.* **2018**, DOI: 10.1021/acscentsci.7b00607.

(2) Chapovetsky, A.; Do, T. H.; Haiges, R.; Takase, M. K.; Marinescu, S. C. Proton-Assisted Reduction of CO_2 by Cobalt Aminopyridine Macrocycles. *J. Am. Chem. Soc.* **2016**, *138* (18), 5765−5768.

(3) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. Electrocatalytic reduction of carbon dioxide by nickel cyclam2+ in water: study of the factors affecting the efficiency and the selectivity of the process. *J. Am. Chem. Soc.* **1986**, *108* (24), 7461−7467.

(4) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. A Local Proton Source Enhances CO_2 Electroreduction to CO by a Molecular Fe Catalyst. *Science* **2012**, *338* (6103), 90−94.

(5) Cardenas, A. J. P.; Ginovska, B.; Kumar, N.; Hou, J.; Raugei, S.; Helm, M. L.; Appel, A. M.; Bullock, R. M.; O'Hagan, M. Controlling Proton Delivery through Catalyst Structural Dynamics. *Angew. Chem., Int. Ed.* **2016**, *55* (43), 13509−13513.

(6) Hammes-Schiffer, S. Proton-Coupled Electron Transfer: Moving Together and Charging Forward. *J. Am. Chem. Soc.* **2015**, *137* (28), 8860−8871.

(7) Keith, J. A.; Grice, K. A.; Kubiak, C. P.; Carter, E. A. Elucidation of the Selectivity of Proton-Dependent Electrocatalytic CO_2 Reduction by fac-Re(bpy)(CO)$_3$Cl. *J. Am. Chem. Soc.* **2013**, *135* (42), 15823−15829.

(8) Azcarate, I.; Costentin, C.; Robert, M.; Savéant, J.-M. Through-Space Charge Interaction Substituent Effects in Molecular Catalysis Leading to the Design of the Most Efficient Catalyst of CO_2-to-CO Electrochemical Conversion. *J. Am. Chem. Soc.* **2016**, *138* (51), 16639−16644.

(9) Parkin, A.; Seravalli, J.; Vincent, K. A.; Ragsdale, S. W.; Armstrong, F. A. Rapid and Efficient Electrocatalytic CO_2/CO Interconversions by Carboxydothermus hydrogenoformans CO Dehydrogenase I on an Electrode. *J. Am. Chem. Soc.* **2007**, *129* (34), 10328−10329.

(10) Jeoung, J.-H.; Dobbek, H. Carbon Dioxide Activation at the Ni,Fe-Cluster of Anaerobic Carbon Monoxide Dehydrogenase. *Science* **2007**, *318* (5855), 1461−1464.