

IV.H.16 Activation of Small Molecules with Bi-Functional Ambiphilic Catalyst Complexes

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Objectives

The objective of our research is to develop fundamental insight into small molecule activation in molecular complexes that will provide the basis for developing rational approaches in new catalysis design. Our focus is bi-functional – ambiphilic catalyst centers – molecular complexes comprised of both electron-rich and electron-poor sites. We are interested in the development of catalyst structures capable of multiply reactions ranging from the heterolytic activation of hydrogen, important for obtaining high selectivity's in the reduction of molecular structures found in biomass, to the direct activation of CO and CO₂ for conversion to energy storage materials.

Technical Barriers

- Tuning thermodynamics and kinetics of ambiphilic molecular complexes to enhance catalytic efficiency.
- Controlling structure and reactivity to enable catalysis of a wide range of substrates in a wide range on environments.

Abstract

Five years ago few chemists would have predicted that molecular hydrogen could be activated at ambient temperature and pressure using a combination of an amine or phosphine Lewis base with a borane Lewis acid. The accepted view had been that metals and d-electrons are required to activate hydrogen [1]. However, a paradigm shift in our appreciation of hydrogen activation and catalysis was initiated by the reports from the Stephan group [2] that a *frustrated Lewis pair* (FLP) – that is, an ambiphilic complex of a Lewis acid and Lewis base that cannot form a formal Donor – Acceptor dative bond provides a *vacancy* of latent reactivity, between the D and A to heterolytically activate

molecular hydrogen – at room temperature. Recently the collaborative efforts by Stephan & Erker [3,4] and Soós & Papai [5] have demonstrated the use of FLP's in catalytic hydrogenation of polar functional groups. The novel reactivity afforded by a bi-functional catalyst, illustrated in Figure 1, demonstrates that there are new approaches to catalysis and small molecule activation that do not require metals [6].

Recent computational studies suggested a few intriguing proposals to describe the unique reactivity of FLPs; Pápai and co-workers suggested that a *reactive pocket* is formed in loosely organized frustrated pair at an optimal acid-base distance providing bifunctional cooperativity for a synergistic interaction with molecular hydrogen [7]. Wang and co-workers suggest that *geometrical constraints* are important and optimal alignment of the Lewis acid and Lewis base can lower the activation barrier [8]. Pyykko describes an energy decomposition analysis (EDA) of H₂ activation by a FLP suggesting the attraction between the protonic and hydridic hydrogen in the products compensates for the energy required to split H₂ homolytic [9]. Finally, Grimme has put forth a provocative hypothesis – that the molecular or chemical nature of the FLP is not as important as the strong electrostatic attraction induced by the FLP [10]. He notes that the *electric field strength* in FLPs approaches the magnitude required to split H₂ in a vacuum without a barrier and that

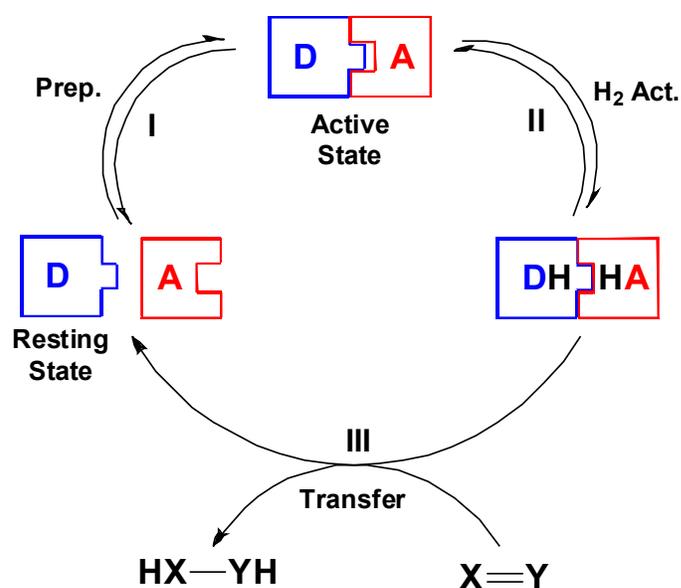


FIGURE 1. Illustration of the catalytic reduction cycle; step I, catalyst preparation; step II, H₂ activation; step III, H₂ transfer.

the rate limiting step for H₂ activation is diffusion into a *prepared Lewis pair* (PLP).

This recent computational work provides some thought-provoking propositions to explain the latent reactivity afforded by bringing together an electron-rich Lewis base and an electron-deficient Lewis acid species – this creates a new reactive *vacancy*. However, there is little experimental insight into either the thermodynamics or kinetics of FLP formation, H₂ activation by FLPs or H₂ transfer from FLPs to unsaturated substrates. **A central theme to our catalysis research program is to minimize the heights of the hills and the depths of the valleys along the reaction pathway.** To this end, we use methods to determine reaction thermodynamics to understand the factors that control the depth of the valleys and measure activation barriers to understand the factors that control the height of the hills in the catalytic reaction cycle. Further to this understanding there are a number of fundamental scientific questions that we will address in our research to maximize the potential of the catalytic cycle outlined in Figure 1:

- Is a sufficient electric field all that is necessary for H₂ activation or are bonding and other environmental factors just as important? Are there geometrical constraints, e.g., specific angles and distances between the Lewis acid and Lewis base to enhance reactivity, both H₂ activation and catalytic H₂ transfer?
- How does the reactivity of a bidentate Lewis acid or base differ from the reactivity of an intramolecular Lewis acid-base complex?
- What parameters best describe the reactivity created in the vacancy, {}, between the Lewis base, D and Lewis acid, A, pair, i.e., D{}A? What is the rate limiting step in the catalytic reduction of polar molecules; hydride transfer, proton transfer, a concerted H⁺/H⁻ transfer?
- How does this distinctive property, i.e., a quasi-open coordination site, {}, formed between an electron rich and electron poor site, correlate with vacancies and defects in heterogeneous catalysis structures and surfaces composed of Lewis acid and Lewis base sites? What properties in these molecular structures are

essential to understand to enable the building of parallel properties in heterogeneous structures?

- What can we learn from fundamental studies of molecular complexes of FLPs combined with transition metals, i.e., ‘tri-functional’ sites to build new catalysts complexes, heterogeneous and homogeneous complexes for small molecule activation and catalysis?
- How general is this phenomena of small molecule activation without metals? How can these *reactive pockets* be optimized for the catalytic reduction of CO₂ or biomass functions, e.g., carbonyls?

Fundamental understanding of novel approaches to catalysis and small molecule activation are of direct relevance to research missions supported by the U.S. Department of Energy to enable basic research science to predict and control matter and energy at the electronic, atomic and molecular levels in order to provide foundations for new energy technologies critical to energy, environment and national security.

Progress Report

In previous research we investigated the heterolytic activation of hydrogen in the *non-frustrated* Lewis acid-base pair, i.e., the pedagogical Lewis acid-base pair, ammonia borane and ammonium borohydride.



In this work we made significant progress on understanding the interaction of protonic and hydridic hydrogen bonding interactions (publishing more than 40 papers in the past 6 years). We focused on ammonium borohydride and ammonia borane because of their relevance to hydrogen storage, which seeks to maximize hydrogen content. However, with our new directions towards catalytic activation of hydrogen, other small molecules, e.g., CO₂, N₂, a wide range of new Lewis acid/base catalyst complexes are now open to study.

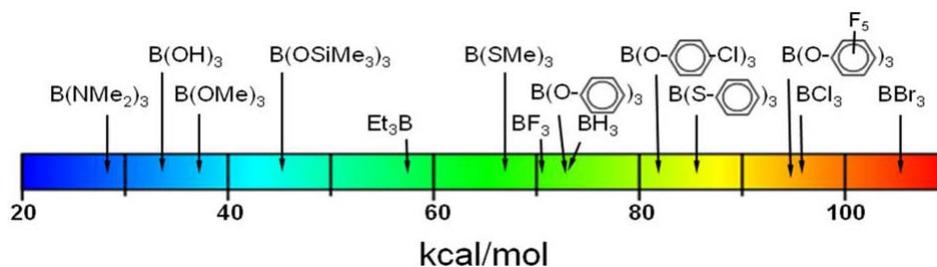


FIGURE 2. Calculated gas phase hydride affinities, ΔH_{HA} , for a series of organic borate esters and BX_3 compounds. Large thermodynamic range, ~ 90 kcal/mol, suggests high degree of tunability for heterolytic hydrogen activation.

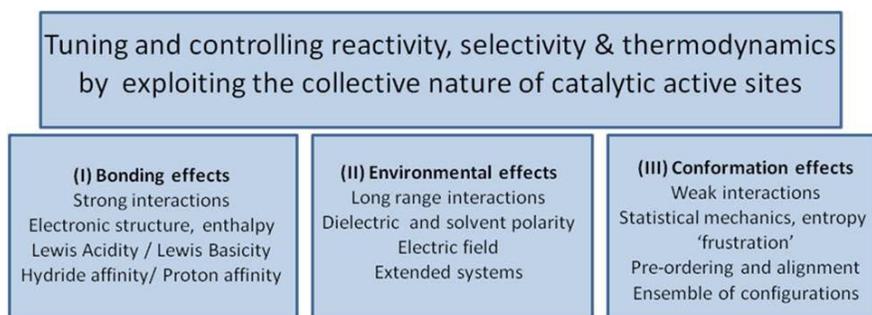


FIGURE 3. Partitioning the effects that give rise to the collective nature of catalysis: (1) bonding, (2) environmental, and (3) conformational factors to determine the reactivity and thermodynamics within an active site. Understand the balance of these factors is a critical bridge between homogeneous and heterogeneous catalysis.

Of direct relevance is the work we performed towards regenerating ammonia borane in which we developed structure reactivity relationships for a series of Lewis acidic borate esters, [11] shown in Scheme 1. This work shows how modification of the structure of the borate ester profoundly affects the hydride affinity of the Lewis acid, a critical parameter that can be tuned to optimize reactivity and thermochemistry of FLPs [12]. Therefore, it is a natural transition for our group to expand the research to investigate small molecule activation within Lewis acid/base pairs using skills and methodologies that we have previously developed.

Future Directions

We are developing a new research task to obtain fundamental insight into the unique reactivity of FLP catalysts. Our proposed research and expertise in thermodynamics and kinetics perfectly complements the ongoing international research in FLP catalysis.

The ultimate goal of our research is to develop predictive models for the rational design of new and novel catalysis systems relevant to DOE missions. Specifically, to develop descriptive models that permits the tuning and control of reactivity of multi-functional catalysis complexes. This will require an in-depth understanding of the factors that control chemical reactivity and thermodynamics in a catalytic active site by characterizing the collective nature of the reacting system, Figure 3. Specifically, a model that describes *bonding, environmental, and conformational factors* in an active site is required to control reactivity and tune thermodynamics. Understanding the balance of these factors can potentially provide a rational bridge between homogeneous and heterogeneous catalysis.

References

1. G Kubas. *Science* **2006**, 314, 1096.
2. GC Welch, RRS Juan, JD Masuda, DW Stephan, *Science* **2006**, 314, 1124.

3. PA Chase, GC Welch, T. Junea, G Erker, DW Stephan, D.W. *Angew. Chem. Int. Ed.* **2007**, 46, 8050.
4. Stephan, D.W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, 49, 46.
5. G Erős, H Mehdi, I Pápai, TA Rokob, P Király, G Tárkányi, T Soós, *Angew. Chem. Int. Ed.* **2010**, 49.
6. PP Power, *Nature* **2010**, 463.
7. Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem.* **2008**, 120, 2469.
8. Lu, G; Li, L.; Zhao, L.; Huang, F.; Wang, Z-X. *Inorg. Chem.* **2010**, 49, 295.
9. Pyykko, P.; Wang, C. *Phys Chem. Chem. Phys.* **2010**, 12, 149.
10. Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, 49, 1402.
11. MT Mock, RG Potter, DM Camaioni, J Li, WG Dougherty, WS Kassel, B Twamley, DL DuBois. *J. Am. Chem. Soc.*, **2009**, 131, 14454
12. GC Welch, L Cabrera, PA Chase, E Hollink, JD Masuda, P Wei, DW Stephan. *Dalton* **2007**, 3407.

Publications (selected) acknowledging the grant or contract

1. Shawn M. Kathmann, Christopher J. Mundy, Gregory K. Schenter, Tom Autrey, Philippe Aeberhard, Bill David, Martin O. Jones, Timmy Ramirez-Cuesta. Understanding Vibrational Anharmonicity and Phonon Dispersion in Solid Ammonia Borane. *J. Phys Chem A*, **2012**, ASAP.
2. Tom Autrey, Mark Bowden, Abhi Karkamkar. Control of hydrogen release and uptake in amine borane molecular complexes: Thermodynamics of ammonia borane, ammonium borohydride, and the diammoniate of diborane. *Faraday Disc.*, **2011**, 151, 157.
3. Mark Bowden and Tom Autrey. Characterization and Mechanistic Studies of the Dehydrogenation of NHxBHx Materials. *Current Opinion in Solid State & Materials Science.* **2011**, 15, 73.
4. Mark Bowden, David J. Heldebrant, Abhi Karkamkar, Thomas Proffen, Gregory K. Schenter, Tom Autrey. The diammoniate of diborane: Crystal structure and hydrogen release. Invited paper for Chem Comm. **2010**, 46, 8564.

5. Abhijeet Karkamkar, Shawn M. Kathmann, Gregory K. Schenter, David J. Heldebrant, Nancy Hess, Maciej Gutowski and Tom Autrey. Thermodynamic and Structural Investigations of Ammonium Borohydride a Solid with a Highest Content of Thermodynamically and Kinetically Accessible Hydrogen. *Chem Materials*, **2009**, 21, 4356.
6. Hyunjeong Kim, Abhi Karkamkar, Tom Autrey, Peter Chupas, Thomas Proffen. Determination of structure and phase transition of light element nanocomposites in mesoporous silica: case study of NH_3BH_3 in MCM-41. *J. Am. Chem. Soc.* **2009**, 131, 13749.
7. Roger Rousseau, Greg Schenter, John Fulton, John Linehan, Tom Autrey. Defining the Active Catalyst Structure and Reaction Pathways from *Ab initio* Molecular Dynamics and *Operando* XAFS: Dehydrogenation of Dimethylaminoborane by Rhodium Clusters. *J. Am. Chem. Soc.* **2009** 131, 10516.
8. Nancy J. Hess, Gregory K. Schenter, Michael R. Hartman, Luc L. Daemen, Thomas Proffen, Shawn M. Kathmann, Christopher J. Mundy, David J. Heldebrant, Ashley C. Stowe and Tom Autrey. Neutron Powder Diffraction and Molecular Simulation Study of the Structural Evolution of Ammonia Borane from 15 to 340 K. *J. Phys Chem. A.* **2009** DOI: 10.1021/jp900839c.
9. Shawn M. Kathmann, Vencislav Parvanov, Gregory K. Schenter, Ashley C. Stowe, Luc L. Daemen, Monika Hartl, John Linehan, Nancy J. Hess, Abhi Karkamkar and Tom Autrey. Experimental and Computational Studies on Collective Hydrogen Dynamics in Ammonia Borane: Incoherent Inelastic Neutron Scattering. *J. Chem Phys*, **2009**, 130, 024507.