

V.N.14 Activation of Small Molecules with Bi-Functional Ambiphilic Catalyst Complexes

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Objectives

To determine and understand the factors controlling the energy landscapes describing the mechanism and the dynamics of catalyzed reaction pathways. Insight into quantitative structure-reactivity relationships will facilitate rational approaches to design and control the synthesis of new catalyst structures.

Technical Barriers

New research tools to measure kinetic and thermodynamic parameters in catalytic reactions. Development of computational methods to study solvent effects on reactions. Discovery of cheaper, *greener* catalyst materials.

Abstract

The objective of our research is to develop fundamental insight into catalysis and 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 centers – molecular complexes comprised of both electron-rich and electron-poor sites, that provide an environment for heterolytic activation of molecular hydrogen and other small molecules such as CO₂ for transformation to fuels for energy storage. Our research approach uses a combination of experimental spectroscopy and computational modeling to study trends in structure-function relationships that control the thermodynamics and kinetics of small molecule activation. The outcome of this research will be predictive models for controlling chemical transformations at the molecular level. This work has wide ranging implications in catalysis for energy storage and energy storage materials as well as alternative approaches

to catalytic activation of small molecules *without using transition metals*.

Progress Report

Until recently, 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 group² 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 & Papai⁵ have demonstrated the use of FLPs 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

While H₂ activation and transfer to polar unsaturated substrates by non-metal catalysts is a provocative observation there is little insight into the mechanism or the properties that control the driving force for the catalytic reaction. In Stephens' pioneering work⁷ it was noted that the reactivity

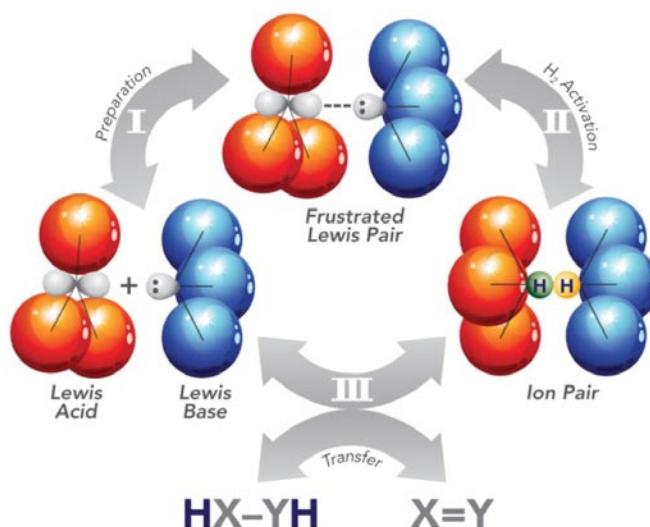


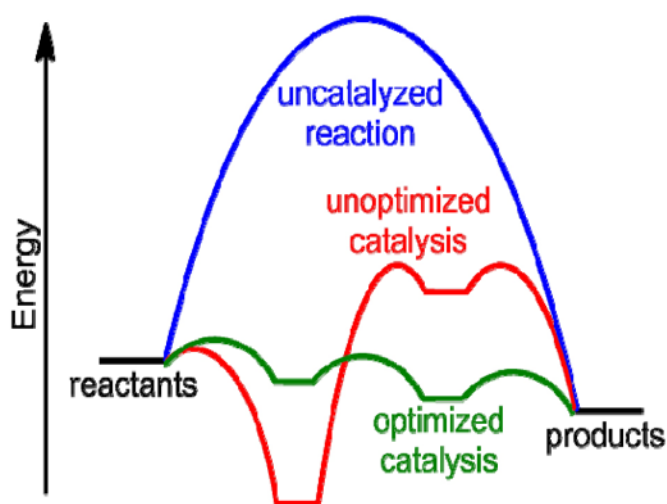
FIGURE 1. Illustration of the catalytic reduction cycle; step I, catalyst preparation; step II, H₂ activation; step III, H₂ transfer.

appeared to be correlated with the cumulative acidity and basicity of the Lewis pairs, however, it was not until recently that Rokob and co-workers provided evidence for this hypothesis.⁸

Recent computational studies suggested a few intriguing proposals to describe the unique reactivity of FLPs; Pápai and co-workers suggested that a loosely organized frustrated pair at an optimal acid-base distance provides *bifunctional cooperativity* for a synergistic interaction with molecular hydrogen.⁹ 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.¹⁰ Pyykko describes an energy decomposition analysis (EDA) of H₂ activation by a FLP and suggests the attraction between the protonic and hydridic hydrogen in the products compensates for the energy required to split H₂ homolytic.¹¹ 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.¹² He notes that the *electric field strength* in FLPs approaches the magnitude required to split H₂ in a vacuum without a barrier and that the rate limiting step for H₂ activation is diffusion into a *prepared Lewis pair* (PLP).

This computational work provides some thought provoking propositions to explain the latent reactivity afforded by bringing together in close proximity an electron rich Lewis base and an electron deficient Lewis acid species creating 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 (*see PI publication list, references 1-3*). 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 geometric 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 and 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 catalyst complexes, heterogeneous & homogeneous complexes for small molecule activation and catalysis?
- How general is this phenomena of small molecule activation without metals? How can these vacancies be optimized for the catalytic reduction of CO₂ or biomass functions, e.g., carbonyls?

These are critical questions relevant to the advancement of hydrogenation catalysis research. The need for novel approaches to catalytic hydrogenation are becoming more important as we consider alternate energy feed stocks – needs ranging from biomass upgrading to the conversion of wastes, e.g., CO₂, to usable liquid fuels, i.e., MeOH. The possibility of the catalytic reduction of carbon dioxide and CO to liquid fuels is not unreasonable given recent reports of reversible binding of CO₂ in FLPs¹³ and the stoichiometric reduction of CO₂ to methanol using an FLP to activate carbon dioxide,¹⁴ or hydrogen.¹⁵ More recently Labinger and Bercaw have demonstrated the synergy of a combination of a metal and Lewis acid/base for the reduction of CO.¹⁶

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.

Future Directions

Our research will build upon our previous accomplishments using experimental spectroscopy, thermodynamic and kinetic measurements combined with computational modeling to gain fundamental insight into the unique properties of bi-functional ambiphilic catalyst centers. We are interested in understanding structure-reactivity relationships for small molecule activation to elucidate the properties that control reactivity (**kinetics**) and driving force (**thermodynamics**) in catalytic reactions. The study of *homotopic*¹⁷ catalytic reaction centers composed of well-defined Lewis acid/base pairs is readily controlled and tunable, both in complexity and function. We will investigate the mechanisms for all steps in the catalytic cycle, (i) catalyst preparation, i.e., the equilibrium between the Lewis acid, A, Lewis base, B, the Frustrated Lewis pair (FLP) and the activated or Prepared Lewis pair (PLP), (ii) H₂ activation by the PLP and (iii) H⁺/H⁻ transfer from the Ionic pair (IP) to the unsaturated substrate, by intra- and inter-molecular and Lewis pairs.

Publication list

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