IV.B.4k Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

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Objectives

- Develop new chemistries to enable DOE to meet the technical objective: "*By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L, and $4/kWh.; by 2015, 3 kWh/kg (9 wt%), 2.7 kWh/L, and $2/kWh*" by using chemical hydrogen storage systems.
- Develop and implement imidazolium-based H_2 activation chemistry.
- Develop and implement systems based on polyhydrides of main group elements: phosphorus, boron, nitrogen.
- Develop and implement cyanocarbon systems for H_2 storage.
- Provide computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE Center of Excellence for Chemical Hydrogen Storage to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(G) Materials of Construction
(J) Thermal Management
(R) Regeneration Processes

Technical Targets

Storage Parameter: DOE 2010 System Targets	Carbene	Cyanocarbon	Phosphacarbons
Material Gravimetric Capacity: 6 wt%	Current: 2% Ultimate: 7.5%	Current: 1% Ultimate: 7.1%	5% with P 7.1% by substituting N for P
Material Volumetric Capacity: 0.045 kg/L	Current: 0.03 Ultimate: 0.098	Current: 0.015 Ultimate: 0.092	Ultimate(P): 0.10 Ultimate(N): 0.092
Dehydrogenation Rate 0.02g/s-kW	In progress	Oxidation step diffusion limited	In progress
Storage Efficiency Center Goal: 50% Near thermoneutral	Exothermic: -5 kcal/mol Ultimate: Thermoneutral	Endothermic: 5 kcal/mol Ultimate: Thermoneutral	Thermoneutral: Estimate

Accomplishments

- Discovered new H_2 storage mechanisms based on the use of H_2O as an additional H_2 source in α,α, α,β, and α,ω eliminations (α,ω mechanisms as being any that are not α,α or α,β).
- Developed concept that a bond is not made in α,α H_2 removal and applied it to α,β, and α,γ eliminations to better manage the thermochemistry and kinetics.

- Developed new synthetic approaches for carbenes for chemical H_2 storage.
- Developed new synthetic approaches for cyanocarbons for chemical H_2 storage.
- Discovered first room temperature uncatalyzed hydrogen storage reaction at carbon.
- Discovered large substituent effect on release of H_2 from nitrogen centers.
- Developed new carbene stability scale for use in designing H_2 storage systems.
- Continue to develop the concept of the importance of ΔG in H_2 storage/release.
- Continued to obtain high quality thermodynamic and mechanistic data for partners.
- Obtained first high quality thermodynamic information on larger borane amine clusters.

Introduction

The focus of the work is the development of new chemistries to enable DOE to meet the technical objective: "By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L (0.045 kg H_2/L), and $4/kWh; by 2015, 3 kWh/kg (9 wt%), 2.7 kWh/L (0.081 kg H_2/L), and $2/kWh" by using chemical hydrogen storage systems. We are: developing and implementing imidazolium-based H_2 activation chemistry; developing and implementing chemical systems based on polyhydrides of main group elements, *e.g.*, phosphorous; developing and implementing cyanocarbon systems for H_2 storage; and providing computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE Center of Excellence for Chemical Hydrogen Storage to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives.

Approach

To achieve the goals described in the Introduction, we are: using novel chemistry approaches to synthesize compounds for easily reversible addition/elimination of H_2 based on our novel, stable carbene chemistry; using first principles computational chemistry approaches on advanced computer architectures to predict the electronic structure of molecules to obtain thermodynamic and kinetic information in support of the design of hydrogen storage materials and of catalysts to effect easy release and addition of H_2; and developing a thermodynamic approach for chemical H_2 storage based on exploiting ΔH and ΔG coupled with Le Chatelier's principle to manage H_2 addition and release in chemical compounds, which is a potential approach for dealing with cold-start issues. For the experimental effort, there are close interactions with the partners LANL and UC-Davis. The computational effort supports the entire Center with special interactions with LANL, PNNL, University of Washington, University of Pennsylvania, UC-Davis, and UCLA.

Results

Substantial progress has been made this year in terms of the experimental and computational efforts. In terms of the experimental work, advances have been made in the areas of: (1) carbene chemistry where we have structurally characterized an imidazolium borohydride, formed carbene·H_2 adducts, isolated carbenium ions in both reduced (hydrogen storage) and oxidized (hydrogen released forms) as shown in Figure 1, and synthesized a polycarbene architecture; (2) cyanocarbon chemistry where we have synthesized a model compound for cyanocarbon·H_2 adducts and isolated a new pyridazine hydrogen storage candidate; and (3) phosphocarbon chemistry where room temperature (uncatalyzed) hydrogen uptake has been achieved as shown in Figure 2.

In terms of the computational work, we have been studying: (1) borane amine reaction mechanisms where we have the first reliable predictions of the energetics of borane amine molecules, developed a model of the chemical bonds and bond energies

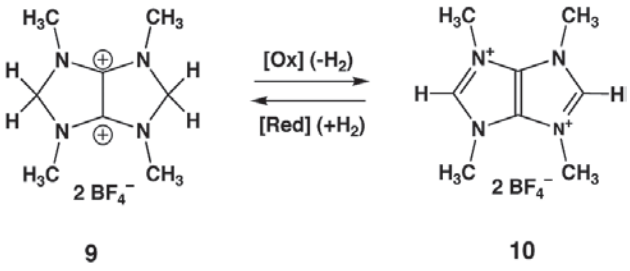

FIGURE 1. Reversible Hydrogen Storage Using Carbenium Cations

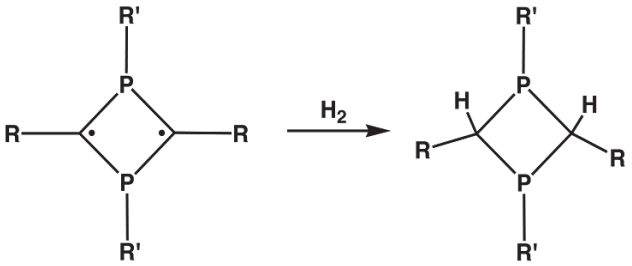

FIGURE 2. Phosphocarbon Molecule for which Uncatalyzed Hydrogen Uptake at Room Temperature has been Achieved

in borane amines, the first predictions of borane amine reaction dehydrogenation kinetics, identified bridging intermediate in borane-amine polymerization mechanism based on calculated nmr chemical shifts, obtained the energetics for isoelectronic compounds, obtained full configuration interaction calculations on states of diatomics to benchmark our methods, and predicted the heats of formation of borane amine salts; (2) borane amine regeneration chemistry where we have the first reliable and extensive predictions of the energetics for regeneration reactions; (3) carbene and cyanocarbon chemistry where we have the first reliable predictions of the energetics of carbenes, discovered a new scale for defining carbene reactivity, the first reliable predictions of the energetics of model nitrogen based compounds, and discovered an organic substituent effect stabilizing H_2 release at N; and (4) the first reliable predictions of bond energies in borane silanes.

Conclusions and Future Directions

We have made substantial progress in the development of new chemistries and computational approaches to meet the DOE needs. We have developed new conceptual models for improving weight percent beyond 1:1 stoichiometry to enable us to meet DOE 2015 goals, developed a thermodynamic approach to meet desorption temperature and plateau pressures, developed carbene and carbenium ion chemistry to meet DOE 2010 goals, and developed new cyanocarbon chemistry to meet DOE 2010 goals. Electronic structure methods were used to successfully predict reliable values of the thermodynamic, kinetic, and spectroscopic properties of compounds for chemical hydrogen storage for the design of new molecular based systems with a focus on carbenes and cyanocarbons, borane amines and isoelectronic molecules, borane amine H_2 release reaction mechanism, and boraneamine regeneration mechanisms.

Our experimental chemistry goals include: (1) continue synthesis and characterization of cyanocarbons for H_2 storage to develop molecules with improved weight percent and as structural components and to extend newly discovered pyridazine chemistry to improve performance and weight percent hydrogen; (2) continue synthesis and characterization of carbenes to improve performance and weight percent hydrogen; (3) continue studies on imidazol(in)ium borohydrides and carbene-borane adducts; (4) develop improved synthesis of and continue characterization of newly discovered phosphocarbons for improved hydrogen release characteristics; (5) initiate expanded studies supporting the extended α,ω -hydrogen storage mechanisms; (6) initiate experimental work on cyclo-PCPC α,γ hydrogen uptake; and (7) extend water activation work to provide more hydrogen by weight (see Figure 3). Our computational chemistry goals include: (1) predict thermodynamics and kinetics for a range of chemistries including borane amine reactions (e.g., ionic pathways) to optimize and control the H_2 release process, 5-step reprocessing approach for optimal B-O to B-H conversion, carbenes and cyanocarbons including pyridazines, and phosphocarbons; (2) develop approaches to predict intermolecular interactions and heats of vaporization/fusion to complete studies of borane amine thermodynamics; (3) use computational approaches to design new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metals; and (4) predict spectroscopic properties (nuclear magnetic resonance, infrared/Raman, ultraviolet-visual) for analyzing experimental data.

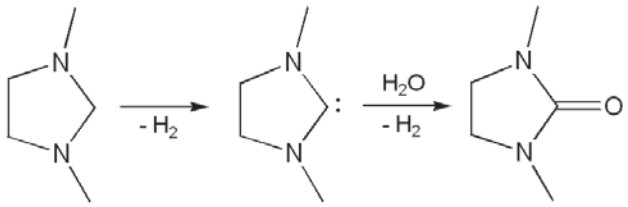

FIGURE 3. Carbene Hydrolysis can Extend Hydrogen Release to Improve the Weight Percent Stored

Special Recognitions & Awards/Patents Issued

1. Keith Bentley, undergraduate student with Arduengo, Deutscher Akademischer Austauch Dienst (DAAD) Fellowship, Summer 2006.

2. Daniel Grant, graduate student with Dixon, Alabama Power Fellowship.

FY 2006 Publications/Presentations

1. "Heats of Formation of the Arduengo Carbene and Various Adducts Including H_2 from Ab Initio Molecular Orbital Theory," D. A. Dixon and A. J. Arduengo, III, *J. Phys. Chem., A*. **2006**, *110*, 1968.

2. "Thermodynamic Properties of Molecular Borane Phosphines, Alane Amines, and and Phosphine Alanes and the $[BH_4^-][PH_4^+]$, $[AlH_4^-][NH_4^+]$, and $[AlH_4^-][PH_4^+]$ Salts for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory," D. J. Grant and D. A. Dixon *J. .Phys. Chem., A*. **2005**, *109*, 10138.

3. "Thermodynamic Properties of the C_5, C_6, and C_8 n-Alkanes from Ab Initio Electronic Structure Theory," L. Pollack, T. L. Windus, and W. A. de Jong, and D.A. Dixon, *J. Phys. Chem. A*, **2005**, *109*, 6934.

4. "Thermodynamic Properties of Molecular Borane Amines and the $[BH_4^-][NH_4^+]$ Salt for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory," D. A. Dixon and M. Gutowski, *J. Phys. Chem. A*, **2005**, *109*, 5129.

5. Invited Lecture, "High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems, hydrocarbon fuels, and main group chemistry," Structure and Function in Chemistry and Biology, Symposium Celebrating the 85th Birthday of Prof. William N. Lipscomb, Shanghai, China, August 2005.

6. Invited Lecture, "Applications of electronic structure theory at the teraflop level and beyond," Computational Chemistry at the Teraflop and Beyond Symposium, ACS National Meeting, Washington, D.C., August 2005.

7. Invited Lecture, Computational studies of metal oxide clusters and catalytic reactions," XVI Undergraduate Research Symposium, Nanotechnology, Computational Chemistry, and Computational Biology Workshop, San Juan, Puerto Rico, September 2005.

8. Invited Lecture, Pacific Chem 2005, "Computational inorganic fluorine chemistry," Inorganic Fluorine Chemistry: From Basic Research to Applications, Honolulu, HI, December 2005.

9. Invited Lecture, Pacific Chem 2005, "New architectures in carbene chemistry," Symposium on Imidazole cyclophanes and Imidazolium ions, Honolulu, HI, December 2005.

10. Invited Lecture, "Computational Thermochemistry," Quantitative Quantum Chemistry, Symposium in honor Thom Dunning, Santa Fe, NM, March 2006.

11. Invited Lecture, "Computational Approaches to the prediction of reaction kinetics for catalysis and chemical hydrogen storage," Solvay Three Day Symposium on Chemical Reactivity, Brussels, April 2006.

12. Tutorial on Hydrogen Storage, "Computational Chemistry for H_2 Storage: Theoretical Background and Applications," Materials Research Society Annual Spring Meeting, April 2006.

13. Invited Lecture, "High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems," Symposium on Advances in Hydrogen Storage, Materials Research Society Annual Spring Meeting, April 2006.

14. Invited Lecture, "High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems," Theory Focus Session on Hydrogen Storage Materials, U.S. DOE H_2 Review Meeting, Crystal City, VA, May 2006.