IV.B.1i Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

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Contract Number: DE-FC36-05GO15059

Start Date: January 1, 2005
Projected End Date: December 31, 2009

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.
- Focus on organic and main group compounds to enable new chemistries which may be able to perform better for release and regeneration of spent fuel by improving the energy balance and to provide longer term alternatives.
- Develop and implement imidazolium (carbene)/cyanocarbon-based H_2 storage systems.
- Provide computational chemistry support (prediction of thermodynamics, kinetics, spectroscopic properties, mechanisms, etc.) 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. Focus on new materials, hydrogen release mechanisms, and regeneration of spent fuel processes.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) 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
(J) Thermal Management
(R) Regeneration Processes

Technical Targets

Storage Parameter: DOE 2010 System Targets	Carbene/ Cyanocarbon	Imidazolo Borane
Material Gravimetric Capacity: 6 wt%	Current: 2% Ultimate for $C_2N_2H_6$ polymer: 10.3%	Current: 1% Ultimate: 8.1%
Material Volumetric Capacity: 0.045 kg/L	Current: 0.045 Ultimate: 0.098	Current: ~0.02 Ultimate: 0.098
Dehydrogenation Rate 0.02 g/s-kW	In progress for polymer	Rate of H_2 release: $9.6 \pm 0.5\ M^{-1}s^{-1}$
Storage Efficiency Center Goal: 50% Near thermoneutral	Exothermic: -5 kcal/mol Ultimate: Thermoneutral	In progress

Accomplishments

- Predicted reliable thermodynamics for >500 reactions for regeneration schemes.
  - Enabled reliable efficiency estimates and improvements in efficiencies to near 90% to help guide experimental studies within the Center of Excellence.
- Made significant advances in reliable predictions of the thermodynamics of new H_2 chemical hydrogen storage systems. Examples:
  - $C_xB_yN_zH_{12}$ (x+y+z = 6) chemistries.
  - Methyl substituted amine-boranes for improved fuel properties (liquids) and improved thermochemistry.

- Developed models of new catalytic and H_2 release processes.
  - Predicted orders of magnitude improvement in kinetics.
- Developed new understanding of alane chemistries for metal hydride regeneration schemes based on amine complexation.
  - Identified multiple transition states and new complexes.
- Developed improved models for carbene/tetracyanoethylene (TCNE) thermochemistry.
  - Enabled the choice of new chemistries.
- Demonstrated cyclization to pure cyclopentamers and cyclohexamers for TCNE/carbene polymers.
- New reduction methodology ($BHCl_2$) under development for TCNE/carbene polymers.
- Imidazole borane chemistry has yielded an imidazole borane adduct that readily releases hydrogen at room temperature. Proof-of-concept validated.

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/cyanocarbon-based H_2 activation chemistry 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. The computational chemistry effort broadly supports the Center in the discovery of new materials, the prediction of novel hydrogen release mechanisms, and the design of efficient regeneration processes.

Approach

To achieve the goals described in the Introduction, we are: (1) developing and identifying new concepts to increase capacity and minimize weight (example: use storage medium for structural benefits); (2) developing new concepts to improve energy balance which is especially relevant for ease of H_2 release and regeneration of the chemical H_2 storage system; (3) developing new approaches to release hydrogen from dihydroimidazoles, based on new chemistry and our world leadership in stable carbene chemistry, and demonstrating proof-of-concepts and key reactions. A key issue is to minimize weight by eliminating substituents or changing them into components that can store H_2 while maintaining kinetic and thermodynamic properties; and (4) using highly accurate first principles computational chemistry approaches (both molecular orbital theory and density functional theory-based) 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 of H_2 as well as efficient regeneration schemes. We are continuing to develop computational thermodynamic and kinetic approaches 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. For the experimental effort, there are close interactions with Los Alamos National Laboratory. The computational effort supports the entire Center.

Results

Substantial progress has been made this year in terms of the experimental and computational efforts. Experimental advances include:

(1) A synthetic strategy to an "endless" hydrogen storage polymer has been developed as shown in Figure 1. Cyclization to pure cyclopentamers and cyclohexamers has been accomplished. The reduction of ureas (**2**) to aminals (**3**) has been problematic as the chemistry is different from the unimolecular model chemistry that we previously developed. This area of research is currently being pursued. New reduction methodology is under development to provide samples for testing of H_2 release rates.

(2) Imidazole borane chemistry (Figure 2) has yielded an imidazole borane adduct that readily releases hydrogen at room temperature. Hydrogen release is catalyzed by electrophiles (BH_3) in accord with theoretical models developed by us in previous efforts. New higher capacity compounds are under development as shown in Figure 3. The rate of H_2 release from imidazoloboranes has been measured as $9.6 \pm 0.5\ M^{-1}s^{-1}$. These compounds have the potential to serve as a co-additive to produce liquid fuels like methyl substituted amine boranes.

Computational advances include:

(1) The prediction of reliable thermodynamics for >500 reactions for regeneration schemes. This has enabled reliable estimates of process efficiency as shown by the following equation and improvements

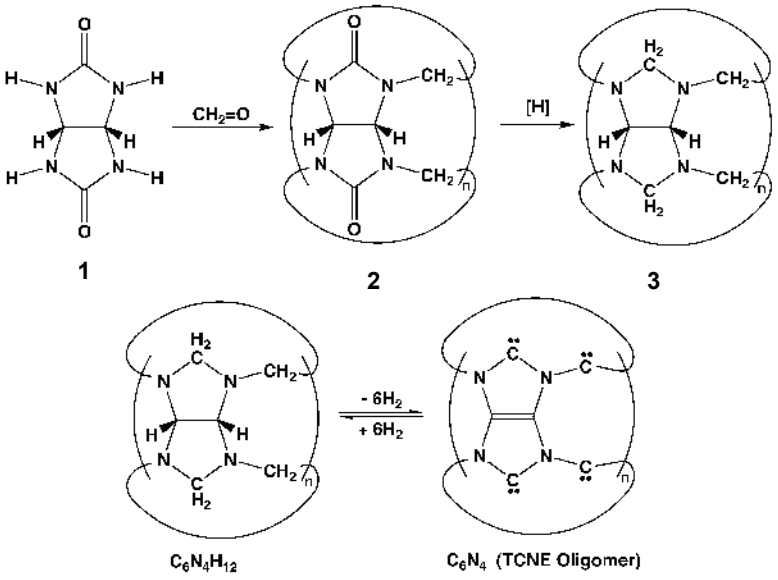

FIGURE 1. Synthetic Approach for the Polymerization of Carbenes to Generate Chemical Hydrogen Storage Materials with Minimal Substituent Weight

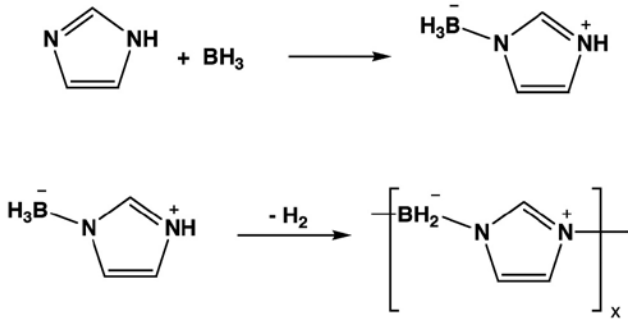

FIGURE 2. Reaction Schemes For Imidazoyl Boranes

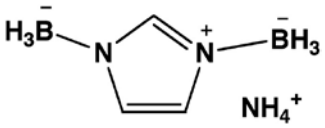

FIGURE 3. Ammomium Boroimidazole Borohydride

in efficiencies to near 90% to help guide experimental studies within the Center of Excellence.

$$\frac{(\text{Equiv. H}_2\text{ stored})(57.8)}{(\text{Equiv. H}_2\text{ used})(57.8)+\sum(\Delta H_{endo})-(\%\text{ heat recovery})\sum(-\Delta H_{exo})}=efficiency$$

A wide range of reactions have been studied and we have studied digestion reactions, reduction reactions, redistribution reactions, hydride recycle reactions, extrusion reactions, and new alternatives to reduction reactions. Our goal is to design a process with a high yield in all steps, which avoids the formation of thermodynamically stable bonds or the formation of diborane (B_2H_6) or NH_3 to increase atom efficiency, recovers and recycles all products, and which minimizes the number of operations. A summary of one potential partially optimized process is shown in Figure 4.

(2) We have made significant advances in reliable predictions of the thermodynamics of new H_2 chemical hydrogen storage systems including $C_xB_yN_zH_{12}$ (x+y+z = 6) chemistries. An example of this chemistry is shown in Figure 5 with ΔG the top value and ΔH the bottom value in kcal/mol for each reaction. The stepwise dehydrogenation energies calculated at the G3(MP2) level of the most stable $B_2N_2C_2H_{12}$ isomer shows that loss of H_2 always occurs from the B-N before the C-C moiety. The final step for loss of H_2 from the CH_2-CH_2 moiety is slightly endothermic due to some aromatic character in the final product. The thermodynamic properties of methyl substituted amine-boranes were predicted reliably for improved fuel properties (liquids) and improved thermochemistry.

(3) We have predicted developed models of new catalytic and H_2 release processes and predicted orders of magnitude improvement in kinetics. This work has led to new understanding of alane chemistries for metal hydride regeneration schemes based on amine complexation where we have identified multiple transition states and new complexes as shown in Figure 6. Alane is a good Lewis acid catalyst because it forms an Al-H--H-N framework with a polar $N^{\delta-}$ $H^{\delta+}$ $^{\delta-}H$ $Al^{\delta+}$ and a double Al-H-B bridge. NH_3 acts a Lewis-base catalyst on Al clusters and forms a linear trimer $NH_3AlH_3NH_3$ which is stable. The zwitterion dimer readily releases H_2.

Conclusions and Future Directions

We have made substantial progress in the development of new chemistries and computational approaches to meet DOE needs for chemical hydrogen storage. We have developed new experimental models for improving weight percent based on convergence in the carbene and cyanocarbon chemistries; designed a new storage system based on imidazolo-borane chemistry; and used highly accurate computational approaches to design new storage systems, predict new release mechanisms and design efficient new regeneration mechanisms.

Our experimental chemistry goals include:

- Synthesize extended carbene polymers (10.3 wt%, oligomer of TCNE ($C_2N_2H_6$)).

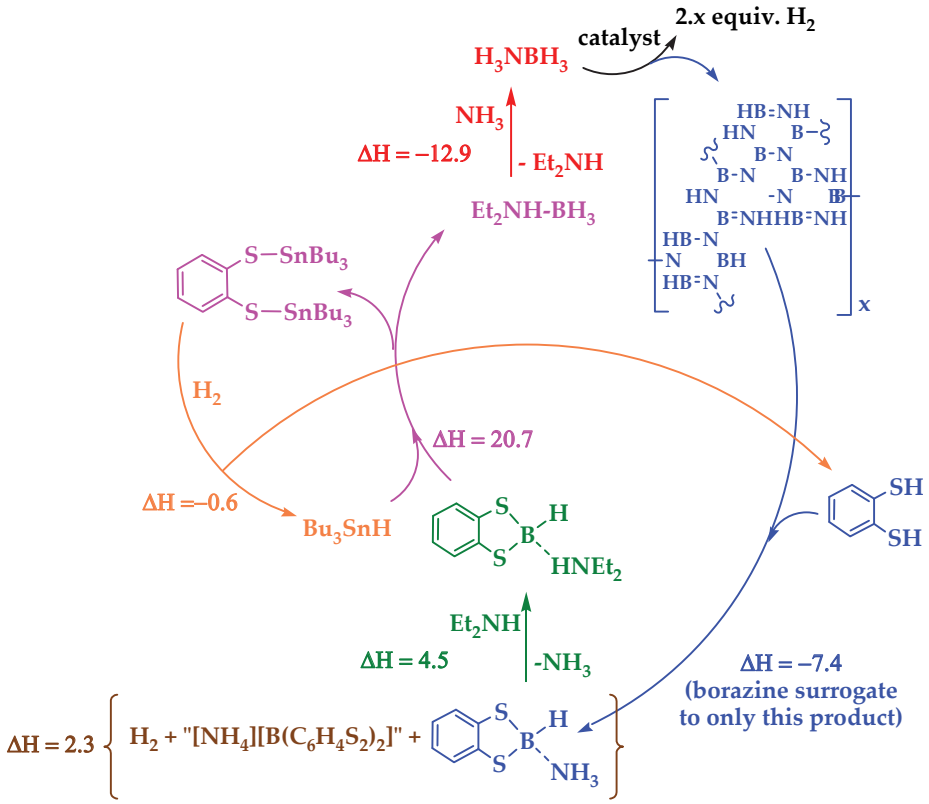

FIGURE 4. Summary of Energetics (kcal/mol) of a Potential Regeneration Scheme Starting from the Products Generated by loss of H_2 from Ammonia Borane with Et_2NH

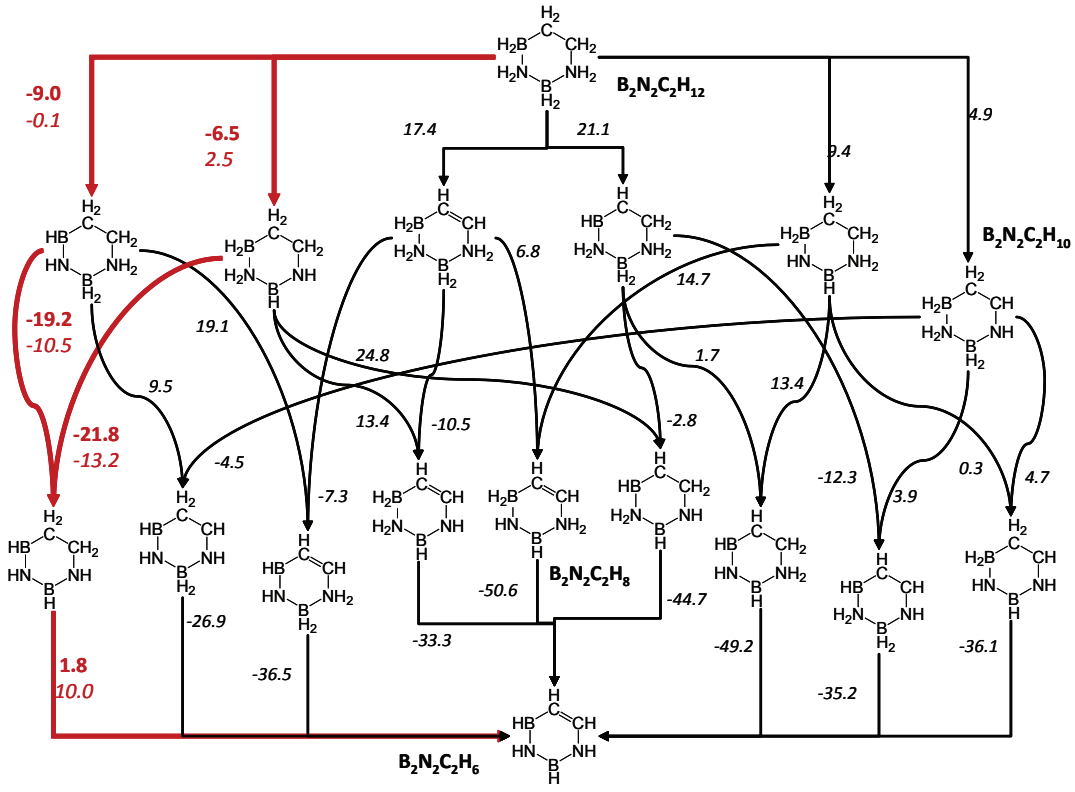

FIGURE 5. Stepwise Dehydrogenation G3MP2 Energies for Loss of H_2 from the most Stable $B_2N_2C_2H_{12}$ Isomer in kcal/mol

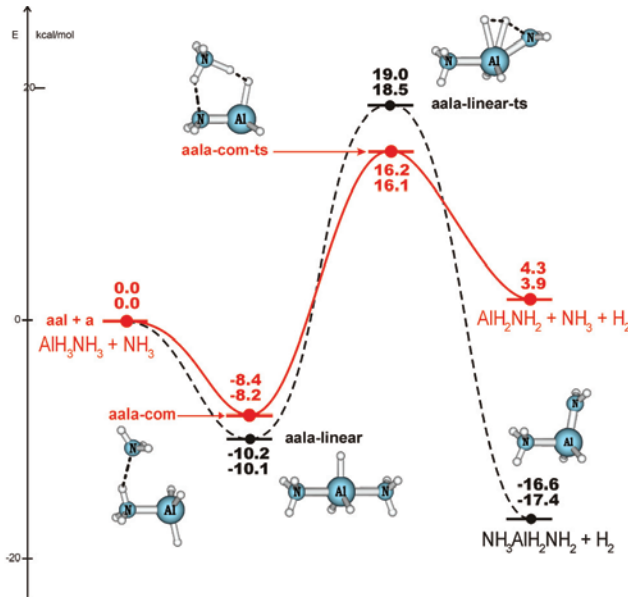

FIGURE 6. Reaction Pathway at the CCSD(T)/Complete Basis Set Level in kcal/mol for the Reaction of NH_3 + AlH_3NH_3

- Improve %H_2 by mass stored in carbene/TCNE systems and in amino(*Imidazolo*)-boranes by reducing substituent mass.
- Improve kinetics for release and regeneration of H_2 for carbene/TCNE systems and in amino(*Imidazolo*)-boranes.

Our computational chemistry goals include:

- Continue to support overall Center efforts in H_2 release, regeneration of spent fuel, and new concepts including alternative inorganic and organic compounds and mechanisms. We will use density functional theory benchmarked by accurate molecular orbital theory methods to calculate thermodynamics and kinetics and to develop reaction mechanisms.
- Use computational approaches to design of new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metal catalysts with specific focus on release and regeneration of spent fuel mechanisms.
- Predict thermodynamics and kinetics for regeneration mechanisms. Predict energetics and rates of key steps (examples: digestion, reduction, etc.) to optimize experimental approach.
- Predict thermodynamics for new ammonia borane (AB) chemistries including new metal/main group BNH compounds $(E(NH_2BH_3)_m$ for activation and AB polymers from anionic polymerization.
- Continue studies of $CBNH_x$ mechanisms to determine underlying physical principles.
- Predict spectroscopic properties for use in analyzing experimental data.

FY 2008 Publications/Presentations

1. "Reliable Predictions of the Thermochemistry of Boron-Nitrogen Hydrogen Storage Compounds: $B_xN_xH_y$, x = 2, 3," M.H. Matus, K.D. Anderson, D.M. Camaioni, S.T. Autrey, and D.A. Dixon, *J. Phys. Chem A.*, **2007**, *111*, 4411.

2. "Ammonia Triborane: Theoretical Study of the Mechanism of Hydrogen Release," V, S. Nguyen, M.H. Matus, M. T. Nguyen, and D.A. Dixon, *J. Phys. Chem A.*, **2007**, *111*, 9603.

3. "Computational Study of the Release of H_2 from Ammonia Borane Dimer $(BH_3NH_3)_2$ and Its Ion Pair Isomers," V.S. Nguyen, M.H. Matus, D.J. Grant, M.T. Nguyen, and D.A. Dixon, *J. Phys. Chem A.*, **2007**, *111*, 8844.

4. "Heats of Formation of Boron Hydride Anions and Dianions and their Ammonium Salts $[B_nH_m^{y-}][NH_4^+]_y$ with y =1 - 2," M.T. Nguyen, M.H. Matus, and D.A. Dixon, *Inorg. Chem*, **2007**, *46*, 7561.

5. "Heats of formation of triplet ethylene, ethylidene, and acetylene," M.T. Nguyen, M.H. Matus, W.A. Lester, Jr., and D. A. Dixon, *J. Phys. Chem. A*, **2008**, *112*, 2082.

6. "Energetics and Mechanism of the Decomposition of Trifluoromethanol" M.T. Nguyen, M.H. Matus, V.T. Ngan, R. Haiges, K.O. Christie, and D.A. Dixon, *J. Phys. Chem. A*, **2008**, *112*, 1298.

7. "Theoretical Study of the Hydrogen Release from Ammonia Alane and the Catalytic Effect of Alane," V.S. Nguyen, M.H. Matus, V.T. Ngan, M.T. Nguyen, and D.A. Dixon, *J. Phys. Chem. C*, **2008**, *112*, 5662.

8. "High Accuracy Computational Studies of Boron-Nitrogen Compounds for Chemical Hydrogen Storage," M.H. Matus, D.J. Grant, S.V Nguyen, K.D. Anderson, M.T. Nguyen, D.M. Camaioni, S.T. Autrey, and D.A. Dixon, *Prepr. Pap.-Am. Chem. Soc., Div.* Fuel *Chem.* **2007**, *52 (2)*, 504.

9. "Computational advances in predicting molecular properties for alternative energy solutions," D.A. Dixon, M.T. Nguyen, M.H. Matus, and S Li, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*. **2008**, *53 (1)*, 105.

10. "Computational Studies on Regeneration of Boron-Nitrogen Compounds for Hydrogen Fuel Cells," M.H. Matus, D.J. Grant, J.R. Switzer, B.L. Davis, F.H. Stephens, and D.A. Dixon, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*. **2008**, *53 (1)*, 115.

11. "Quantum Chemical Studies of Alane and Phosphine Derivatives for Chemical Hydrogen Storage," M.T. Nguyen, S.V. Nguyen, M.H. Matus, D.J. Grant, S. Swinnen, and D.A. Dixon, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*. **2008**, *53 (1)*, 141.

12. Thermochemical Properties of CHFO and CF_2O" by M.H. Matus, M.T. Nguyen, D.A. Dixon, and K.O. Christe, *J. Phys. Chem. A*, **2008**, *112*, 4973.

13. "Reactions of Diborane with Ammonia and Ammonia Borane: Catalytic Effects in Multiple Pathways for Hydrogen Release," V.S. Nguyen, M.H. Matus, M.T. Nguyen, and D.A. Dixon, *J. Phys. Chem.*, accepted July 2008.

14. M.H. Matus and D. A. Dixon, Presentation, *Estudios Computacionales de Compuestos de Boro y Nitrógeno para el Almacenamiento Químico de Hidrógeno,* "Computational Studies Of Boron-Nitrogen Compounds For Chemical Hydrogen Storage", VI Reunión Mexicana de Fisicoquímica Teórica, San Miguel Regla, Hgo., Mexico, November 2007.

15. A.J. Arduengo, "The Evolution of Nucleophilic Carbene Chemistry," Anthony J. Arduengo, III Abschlusskolloquium of the DFG-Schwerpunktprogramm, Münster, Germany, September 28-30, 2007.

16. A.J. Arduengo, "Die jüngsten Carben-Werkzeuge" Anthony J. Arduengo, Heidelberg, Germany, December 17, 2007.

17. A.J. Arduengo, "New Structural Units Based on Imidazol(in)-2-ylidenes - Ligands for Transition Metals and Main Group Elements" Anthony J. Arduengo, Hannover, Germany, December 18, 2007.

18. A.J. Arduengo, "Modifications of Imidazole-Derived Carbenes" Anthony, J. Arduengo, III, Bonn, Germany, December 13, 2007.

19. D.A. Dixon, *Computational Advances in Predicting Molecular Properties for Alternative Energy Solutions*, Introductory talk, Symposium on Computational Methods and Molecular Modeling in Fuel Chemistry, American Chemical Society (ACS), Division of Fuel Chemistry, Spring National Meeting, New Orleans, April 2008.

20. D.A. Dixon, *Computational Advances in Predicting Molecular Properties for Alternative Energy Solutions*, Plenary lecturer, 40th Annual Southeastern Regional American Chemical Society Undergraduate Research Conference, Mississippi, College, Clinton, MS, April 2008.

21. A. Cugini, D.T. Daly, M. Gutowski, D.A. Dixon, and C. Naik, Organizers, Symposium on Computational Methods and Molecular Modeling in Fuel Chemistry, American Chemical Society (ACS), Division of Fuel Chemistry, Spring National Meeting, New Orleans, April 2008 (8 invited talks and 16 contributed talks).

22. M. H. Matus, D.J. Grant, J.R. Switzer, B.L. Davis, F.H. Stevens, and D.A. Dixon, Invited talk, *Computational studies on regeneration of boron-nitrogen compounds for hydrogen fuel cells*, Symposium on Computational Methods and Molecular Modeling in Fuel Chemistry, American Chemical Society (ACS), Division of Fuel Chemistry, Spring National Meeting, New Orleans, April 2008.

23. M.T. Nguyen, M.H. Matus, D.J. Grant, S.V. Nguyen, S. Swinnen, and David A. Dixon, Invited talk, *Quantum chemical studies of alane and phosphine derivatives for chemical hydrogen storage*, Symposium on Computational Methods and Molecular Modeling in Fuel Chemistry, American Chemical Society (ACS), Division of Fuel Chemistry, Spring National Meeting, New Orleans, April 2008.

24. D.A. Dixon, *Computational Approaches to the Prediction of Molecular Properties for Chemical Hydrogen Storage*, Plenary lecture, Hydrogen Symposium 2008, Purdue University, April 2008.

25. M.H. Matus, D.J. Grant, J. R. Switzer, B.L. Davis, F.H. Stephens, and D.A. Dixon, *Computational Studies on Regeneration of Boron-Nitrogen Compounds for Hydrogen Fuel Cells,* 37th Annual Conference of the Southeast Theoretical Chemists' Association, May, 2007, The University of Alabama.