IV.B.1e 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 1.5 kWh/kg (4.5 wt%) and 0.9 kWh/L. By 2015, develop and verify on-board hydrogen storage systems achieving 1.8 kWh/kg (5.5 wt%) and 1.3 kWh/L* by using chemical hydrogen storage systems.
- Focus on novel 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.
- 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 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan: http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(I) Dispensing Technology
(J) Thermal Management
(R) Regeneration Processes
(S) By-Product/Spent Material Removal

Technical Targets

Storage Parameter: DOE 2010 System Targets	Carbene/Cyanocarbon: (No-Go Decision)	Imidazolo Borane
Material Gravimetric Capacity: 4.5 wt%	Current: 2%	Current: 1% Ultimate: 7.1%
Material Volumetric Capacity: 0.028 kg/L	Current: 0.045	Current: ~0.02 Ultimate: 0.098
Dehydrogenation Rate 0.02g/s-kW	In progress	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

- Developed approach to predict heats of vaporization (liquid heats of formation) with new atomic parameters derived from experiment (Chemical Hydrogen Center of Excellence, Los Alamos National Laboratory, Rohm & Haas). Tested against known values. Used for process simulations.
- Predicted reliable thermodynamics for thousands of compounds for release and regeneration schemes to aid in materials design and process design and simulation. Data provides guidance for experimental design and used in process simulations.

  - Continued validation of density functional theory (DFT) by experiment where available and accurate molecular orbital (MO) theory (coupled cluster theory with single and double excitations plus a perturbative correction for triple excitations/ complete basis set limit).
  - Significant advances in reliable predictions of the thermodynamics of new chemical hydrogen storage systems to help groups focus experimental efforts. Example: Calculated $C_xB_yN_zH_{12}$ (x+y+z = 6) chemistries – new aromatic compound C_4BNH_6.
  - Predicted properties of borane-imidazole complexes with potential to improve release kinetics.
  - Predicted energetics for methyl substituted amine-boranes for improved fuel properties (liquids) and improved thermochemistry. Also for amine exchange reactions for regeneration.
  - Developed new thermodynamic models for metal substituted $M/BH_2NH_3^-$ and $M/NH_2BH_3^-$ complexes. M = Li, Mg, Ca, Al, Si, C, P, N, Ti (Chemical Hydrogen Center of Excellence and University of Missouri).
- Predicted kinetics for a range of H_2 release processes.
  - Extended work to alanes. Identified multiple transition states and new complexes. Interact with Metal Hydride Center of Excellence.
- Carbene experimental work completed. (No-Go decision).
- Exploring different carbon, nitrogen, boron and hydrogen compounds based on BH_3-imidazole structure computationally and new routes to ammonia borane (AB).

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Introduction

Our goal is to develop new chemistries to enable DOE to meet the technical objective: *By 2010, develop and verify on-board hydrogen storage systems achieving 1.5 kWh/kg (4.5 wt%) and 0.9 kWh/L. By 2015, develop and verify on-board hydrogen storage systems achieving 1.8 kWh/kg (5.5 wt%) and 1.3 kWh/L* by using chemical hydrogen storage systems. We are: providing computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE Chemical Hydrogen Storage Center of Excellence 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. We are using experimental approaches to synthesize new organic/main group compounds with the appropriate release kinetics and thermodynamics and that can be readily regenerated.

Approach

To achieve the goals described in the Introduction, we are:

1. Using highly accurate and validated 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 regeneration systems. Our focus is on the design of hydrogen storage materials and of catalysts to effect easy release of H_2 as well as efficient regeneration schemes. We use a combination of validated MO theory and DFT based on our accurate benchmark calculations. We are developing methods to predict the properties of the molecules under study in condensed phases. The key issue is the accuracy/ reliability of the models for the real systems.
2. Developing new compounds and approaches to release hydrogen from organic and main group compounds based on new chemistries. The focus of this effort is to demonstrate proof of concepts and key reactions. The key experimental issues are minimizing the weight by eliminating substituents or changing them into components that can store H_2 while maintaining kinetic and thermodynamic properties and demonstrating H_2 release reactions under expected operating conditions.
3. Using a combined computational/experimental goal to develop new concepts to improve energy balance which is relevant for the ease of H_2 release and regeneration of H_2 storage system. 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 computational and experimental efforts.

Examples of computational results include:

1. The prediction of reliable thermodynamics for thousands of compounds for release and

regeneration schemes to aid in materials design and process design and simulation. All of our thermodynamic values have been updated due to a new heat of formation of the B atom. We developed and tested extensively a validated, new approach for the prediction of molecular properties in condensed phases with new atomic parameters to predict T_{BP}, ΔH_{vap}, and ΔH(liquid) which uses accurate calculated ΔH(gas) and is based on the computational method COnductor like Screening MOdel for Realistic Solvents (COSMO-RS). Thermodynamic and kinetic data was provided to experimentalists to guide their choice of experiments. Thermodynamic and property data was provided to Rohm & Haas (Dow) for the chemical process simulations at the plant level for regeneration and first fill. An example of such data is shown in Figure 1. We developed a good model for the prediction of the thermodynamics of spent fuel for "BNH_2" and "BNH". Reliable estimates of maximum process efficiency in terms of thermodynamics was made using equation (1)

$$\frac{(\text{Equiv. H}_2\text{ stored})(57.8)}{(\text{Equiv. H}_2\text{ used})(57.8)+\sum(\Delta H_{endo})-(\%\text{ heat recovery})\sum(-\Delta H_{exo})}=\textit{efficiency} \quad (1)$$

2. We have made significant advances in reliable predictions of the thermodynamics of new H_2 chemical hydrogen storage systems including those based on the product C_4BNH_6. A reliable heat of formation of C_4BNH_6 at 298 K of 3.0 kcal/mol was predicted and the compound is shown to have a resonance stabilization energy of 21 ± 2 kcal/mol in comparison to a value of 34.1 kcal/mol for benzene obtained in the same way (collaboration with the University of Oregon).
3. We have extended our computational studies to complexes of borane amines bonded to main group compounds and transition metals. An important set of main group and transition metal complexes are derived from binding $(NH_2BH_3)^-$ to a cationic center such as Li^+, Ca^{2+}, Al^{3+} or Ti^{4+} to form the respective complexes $Li(NH_2BH_3)$, $Ca(NH_2BH_3)_2$, $Al(NH_2BH_3)_3$, and $Ti(NH_2BH_3)_4$. We are completing such calculations as well as on the reverse compositions based on $M\text{-}(BH_2NH_3)_n$. Calculations have been done for a number of molecular systems at the DFT (B3LYP) and MO theory (G3MP2) levels. An example is shown in Figure 2.
4. We have continued our studies of catalytic 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. This has also been extended to reactions of hydrazine as shown in Figure 3.

Experimental advances include:

1. A borane transfer process has been developed based on a du Pont patent (No. 5,034,464; A.J. Arduengo, July 23, 1991). The new process facilitates transfer of a BH_3 unit from sodium borohydride to a variety of amines (including ammonia) with the intermediary of a proprietary borane transfer agent as shown in Figure 4. The overall yield in early experiments is 80–95%.

Reactor 1:		
ΔH(kcal/mol)		
Digestion	**(1a)** $BNH + 1.5\ C_6H_4(SH)_2 \rightarrow 0.5\ HB(C_6H_4S_2){\cdot}NH_3 + 0.5\ (NH_4)B(C_6H_4S_2)_2$	8.6
Undesirable:	**(1b)** $C_6H_4(SH)_2 + HB(C_6H_4S_2){\cdot}NH_3 \rightarrow (NH_4)B(C_6H_4S_2)_2 + H_2$	22.9
Reactor 2:		
Reduction:	**(2a)** $0.5\ (NH_4)B(C_6H_4S_2)_2 + 0.5\ Bu_3SnH \rightarrow 0.5\ HB(C_6H_4S_2){\cdot}NH_3 + 0.5\ (C_6H_4)(SH)(SSnBu_3)$	-18.3
Amine Exchange:	**(2b)** $HB(C_6H_4S_2){\cdot}NH_3 + Et_2NH \rightarrow HB(C_6H_4S_2){\cdot}NHEt_2 + NH_3(g)$	1.6
Reduction:	**(2c)** $HB(C_6H_4S_2){\cdot}NHEt_2 + 2\ Bu_3SnH \rightarrow Et_2NHBH_3 + C_6H_4(SSnBu_3)_2$	9.5
Net:	**(2d)** $0.5\ HB(C_6H4S_2){\cdot}NH_3 + 0.5\ (NH_4)B(C_6H_4S_2)_2 + Et_2NH + 2.5\ Bu_3SnH \rightarrow Et_2NHBH_3 + NH_3 + 0.5\ (C_6H_4)(SH)(SSnBu_3) + C_6H_4(SSnBu_3)_2$	-7.2
Undesirable:	**(2e)** $C_6H_4(SH)_2 + Bu_3SnH \rightarrow C_6H_4(SH)(SSnBu_3) + H_2$	-13.7
	(2f) $C_6H_4(SH)(SSnBu_3) + Bu_3SnH \rightarrow C_6H_4(SSnBu_3)_2 + H_2$	-5.0
Net:	(2g) $C_6H_4(SH)_2 + 2Bu_3SnH \rightarrow C_6H_4(SSnBu_3)_2 + 2H_2$	-18.7
Reactor 3		
Ammoniation:	(3) $Et_2NHBH_3 + NH_3\ (l) \leftrightarrows H_3NBH_3 + Et_2NH$	-7.3
Reactor 4:		
Metal Recycle:	(4a) $C_6H_4(SSnBu_3)_2 + 2H_2 \rightarrow C_6H_4(SH)_2 + 2\ Bu_3SnH$	18.7
	(4b) $0.5\ C_6H_4(SH)(SSnBu_3) + 0.5\ H_2 \rightarrow 0.5\ C_6H_4(SH)_2 + 0.5\ Bu_3SnH$	6.8

FIGURE 1. Thermodynamics in kcal/mol for Los Alamos National Laboratory AB regeneration pathway. Thermodynamic data enables process simulations and cost estimates.

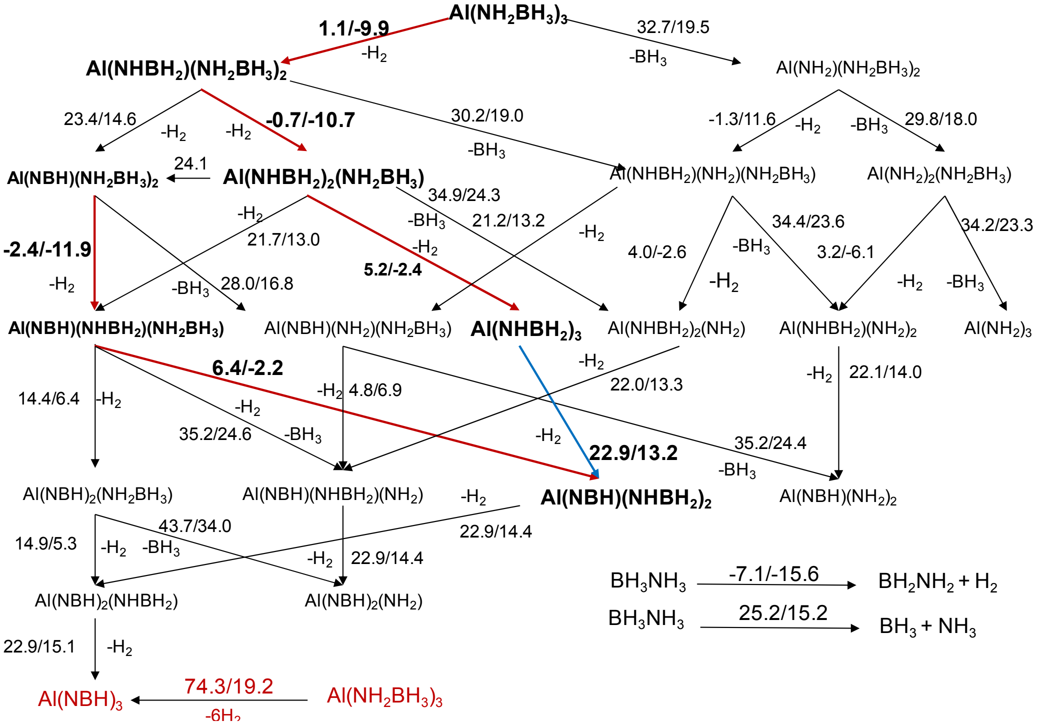

FIGURE 2. Dehydrogenation pathways and B-N bond dissociation energies for the aluminum borane amines at the B3LYP/DZVP2 level. ΔH(298)/ΔG(298) in kcal/mol are given.

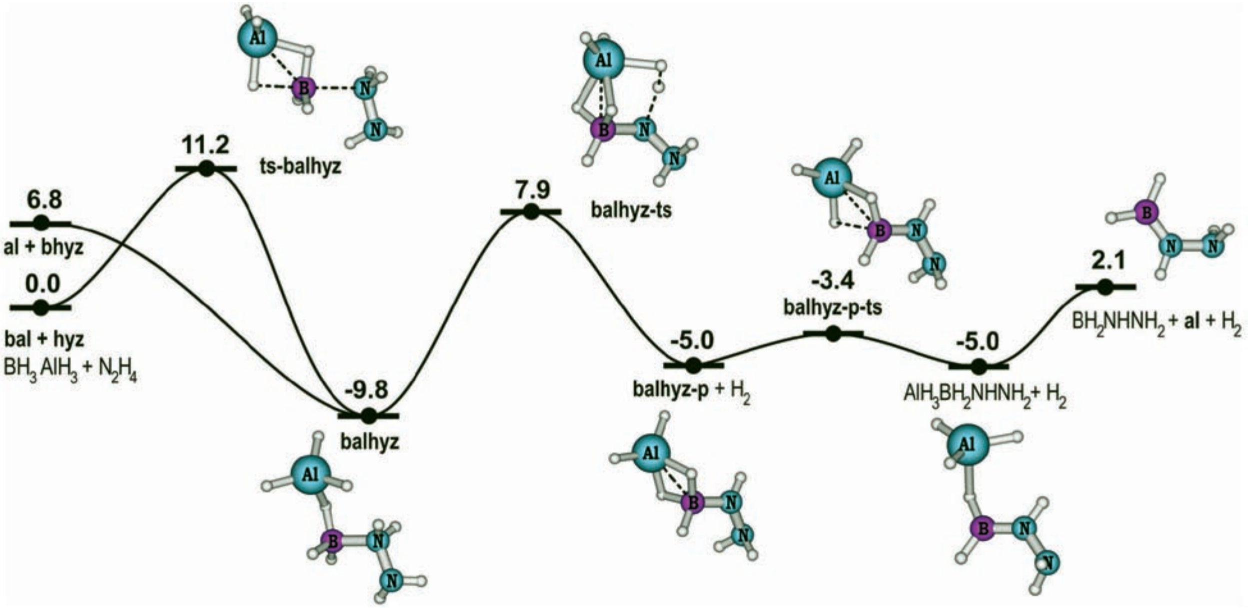

FIGURE 3. Energy profiles showing the pathways for H_2-release from AlH_3 + BH_3 + N_2H_4. Relative energies in kcal/mol at the CCSD(T)/aVTZ + ZPE level. Small balls are H atoms.

2. A novel hydrogen activation process has been developed which showed that Lewis acid-base pairs need not be "frustrated" in their reactivity towards activating H_2. Reaction can occur at temperatures as low as -80°C. We established that the interaction of H_2 with the electrophile is a key step in the

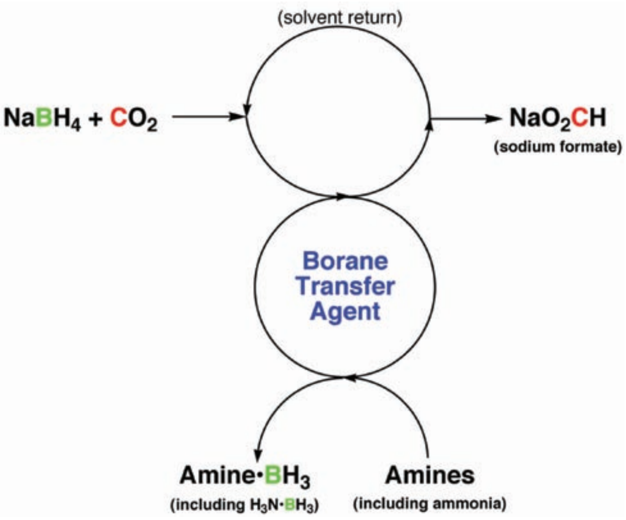

FIGURE 4. Schematic of borane transfer technology for new approach to the synthesis of first fill ammonia borane.

activation process. Electrophiles to replace our initial $Fe(CO)_5$ reactant such as BBr_3, $B(OCH_3)_3$, 1-bora-adamantane, and trityl cation reacting with an imidazolylidene nucleophile have been investigated. The BBr_3 and trityl cation work. This provides another route to make H_2 into a proton and hydride (like BH_3NH_3) or the Pacific Northwest National Laboratory (PNNL) work for regeneration cycles.

3. We have continued to study hydrogen elimination from azolium borohydrides (polymeric amine borane analogs) from both a computational and experimental viewpoint. The reduced basicity of heterocyclic systems containing multiple nitrogens is such that amine-borane adduct formation from the neutral is difficult and the stability of the initially formed adducts is marginal. Hydrogen evolution was observed during the initial borane complexation step of these reactions. The scope and type of electrophile that can activate dihydrogen in the carbene driven hydrogen storage system is under expansion in order to better manage weight and reactivity in future systems. Recent work has expanded to include (carbonyl)tungsten phosphinidenoids, and phosphenium cations.

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 and used highly accurate computational approaches to design new storage systems, predict new release mechanisms, and design efficient new regeneration mechanisms. We have provided critical data to the process simulations. A new borane transfer process has been developed which facilitates transfer of a BH_3 unit from sodium borohydride to a variety of amines (including ammonia). A novel hydrogen activation process has been developed which showed that Lewis acid-base pairs need not be "frustrated" in their reactivity towards activating H_2.

Our experimental chemistry goals include:

- Continue development of a new route to synthesis of AB for first fill.
- The scope and utility of the novel hydrogen activation especially for regeneration is being further investigated. Experiments with a partner in Bonn, Germany will allow for the study of the reaction in a low temperature autoclave.
- Improve kinetics for release and regeneration of H_2 in amino(*Imidazolo*)-boranes. Expand to include 1,2,4-triazoles and tetrazole. In the next period, obtain stable azole-borane adducts by starting from the more basic azolides (azole-anions).

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 DFT benchmarked by accurate MO theory methods to calculate thermodynamics and kinetics and to develop reaction mechanisms and properties for use in process design simulations as well as overall process efficiencies. We will continue to test the prediction of new molecular properties against available experimental data and improve parameterization schemes.
- Use computational approaches to design 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. We will continue our work in the prediction of Lewis acidities with the PNNL as we have the most extensive set of accurate Lewis acidities available for boron compounds.
- 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 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 (nuclear magnetic resonance, infrared/Raman, ultraviolet-visible) for use in analyzing experimental data.

FY 2009 Publications/Presentations

1. "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.*, **2008**, *112*, 9946.

2. "Poly(Biradicals): Oligomers of 1,3-Diphosphacyclobutane-2,4-diyl Units" Masaaki Yoshifuji, A.J. Arduengo, III, Shigekazu Ito, Joji Miura, and Noboru Morita) *Angew. Chemie, Int. Ed. Engl.*, **2008**, *47*, 6418.

3. "Heats of Formation and Bond Energies of the $H_{(3-n)}BX_n$ compounds for (X = F, Cl, Br, I, NH_2, OH, and SH)," D.J. Grant and D.A. Dixon *J. Phys. Chem. A*, **2009**, *113*, 777.

4. "Diammoniosilane: Computational Prediction of the Thermodynamic Properties of a Potential Chemical Hydrogen Storage System," D.J. Grant, A.J. Arduengo, III, and D.A. Dixon, *J. Phys. Chem. A*, **2009**, *113*, 750.

5. "Coordination of aminoborane, NH_2BH_2, dictates selectivity and extent of H_2 release in metal-catalysed ammonia borane dehydrogenation.," V. Pons, R.T. Baker, N.K. Szymczak, D.J. Heldebrant, J.C. Linehan, M.H. Matus, D.J. Grant, D.A. Dixon*, Chem Comm*., **2008**, 6597.

6. "Studies on stable 1,3-diphosphacyclobutane-2,4-diyls," M. Yoshifuji, A.J. Arduengo, III, and S. Ito, Shigekazu, *Phosphorus, Sulfur and Silicon and the Related Elements*, **2008**, *183*, 335.

7. "A Hybrid Organic/Inorganic Benzene," A.J.V. Marwitz, M.H. Matus, L.N. Zakharov, D.A. Dixon, and S.-Y. Liu, *Angew. Chem. Int. Ed.*, **2009**, *48*, 973.

8. "Thermochemistry and Electronic Structure of Small Boron and Boron Oxide Clusters and Their Anions," M.T. Nguyen, M.H. Matus, V.T. Ngan, D.J. Grant, and D.A. Dixon, *J. Phys. Chem. A*, **2009**, *113*, 4895.

9. "Heats of Formation of the Halosilanes, Methylhalosilanes and Halomethylasilanes from High Level Electronic Structure Calculations," D.J. Grant, and D.A. Dixon, *J. Phys. Chem. A*, **2009**, *113*, 3656.

10. "Catenation of 1,3-diphosphacyclobutane-2,4-diyl units having 2,4,6-tri-tert-butylphenyl protecting groups and a P-sec-butyl group in the ring," S. Ito, J. Miura, N. Morita, M. Yoshifuji, and A.J. Arduengo, III, *Zeitschrift fuer Anorganische und Allgemeine Chemie* **2009**, *635*, 488.

11. "Thermochemistry for the Dehydrogenation of Methyl Substituted Ammonia Borane Compounds," D.J. Grant, M.H. Matus, K.D. Anderson, D.M. Camaioni, S. Neufeldt, C.F. Lane, and D.A. Dixon*, J. Phys. Chem. A*, **2009**, *113*, 6121.

12. "Efficient Regeneration of Partially Spent Ammonia Borane Fuel," B.L. Davis, D.A. Dixon, E.B. Garner, J.C. Gordon, M.H. Matus, and F.H. Stephens, *Angew. Chem*., WEB ASAP, June, 2009.

13. "The Effect of the NH_2 Substituent on NH_3: Hydrazine as an Alternative for Ammonia in Hydrogen Release with Presence of Borane and Alane," V.S. Nguyen, S. Swinnen, M.H. Matus, M.T. Nguyen, and D.A. Dixon, *Phys. Chem. Chem. Phys.*, WEB ASAP, June, 2009.

14. D.A. Dixon and A.J. Arduengo, "Main Group Element Chemistry in Service of Hydrogen Storage and Activation,"DOE Hydrogen Annual Review, Crystal City, June, 2008.

15. D.A.. Dixon, "Fuel Cell & Hydrogen Research at UA," presentation to the Honorable Jeff Sessions, U.S. Senator (AL, R), The University of Alabama, Tuscaloosa, AL, June, 2008.

16. A.J. Arduengo, III, "Imidazol-2-ylidene zu polycyclischen Carbenen: Strukturen, die aus der Reihe tanzen," Kolloquium Münchener Chemische Ges., Ludwigs Maximilians Universität München, Germany, July, 2008.

17. D.A. Dixon, "Computational Chemistry for Design of Materials for Hydrogen Storage, Activation, and Regeneration," Invited presentation, Joint LANL-NEDO Workshop on Hydrogen Storage and Fuel Cells, San Diego, Sept. 2008.

18. D.A. Dixon, "UA Computational Work for the Center of Excellence," Annual Meetig of the DOE Center of Excellence in Chemical Hydrogen Storage, Nov. 8-9, 2008, Denver, CO

19. D.A. Dixon, "New Concepts in the Energetics of Main Group Compounds," Invited Presentation, Main Group and f-Element Chemistry Symposium, Southeastern Regional Meeting of the American Chemical Society (SERMACS), November 14, 2008, Nashville, TN.

20. D.A. Dixon, "Recent UA Computational Work for the DOE Center of Excellence in Chemical Hydrogen Storage," Invited Presentation to the DOE Center of Excellence in Metal Hydrides Meeting, Dec. 18, 2008, California Institute of Technology, Pasadena, CA.

21. D.A. Dixon, invited presentation, "Prediction of Reliable Bond Energies and Molecular Properties for Fluorinated Compounds," 19th Winter Fluorine Conference, St. Petersburg Beach, FL, Jan. 2009.

22. D.A. Dixon, plenary lecture, "Prediction of Reliable Heats of Formation and Bond Dissociation Energies," 49th Sanibel Symposium, Feb. 2009, St. Simons Island, Georgia.

23. D.A. Dixon, Invited lecture, "Computational chemistry for catalysis, hydrogen storage, and the stratosphere," Mississippi State University, March, 2009, Starkville, MS.

24. D.A. Dixon, "Computational Chemistry Support for the DOE CoE in Chemical Hydrogen Storage," Tech Team Review, March 2009, Detroit, MI.

25. A.J. Arduengo, III, "Poly(imidazol(in)ylidene) und Chelatisierende Imidazol(in)ylidene: Entwicklungen aus der Carben-Chemie," Organisch-Chemisches-Kolloquium International, Marburg, Germany (December, 2008).

26. A.J. Arduengo, III, "Neue Ringsysteme und Chelatstrukturen aus Imidazol(in)ylidene," Organic Colloqium International, Gieβen, Germany (December, 2008).