



Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

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Overview

Timeline

- Project start date: Jan. 05
- Project end date: FY10
- Percent complete: 80%

Barriers

DOE Barriers addressed

- System Cost
- System Weight and Volume
- Spent Fuel Regeneration

Budget

- Projected total project funding: \$2,255,397
- DOE share: \$1,649,496(requested)
- UA share: \$605,901
- Funding for FY08: \$370K (DOE)
- Funding for FY09: \$300K (DOE)

Partners

• DOE Center of Excellence for Chemical Hydrogen Storage

• LANL, PNNL, UW, UC-Davis, Penn State, UA, Penn, U. Missouri-Columbia, Millenium Cell, Rohm and Haas, and Rio Tinto.

Objectives/Relevance

 Develop promising approaches to chemical H₂ storage for current and future DOE targets using computational chemistry and synthetic organic/inorganic chemistry.

- 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.*

 Provide computational chemistry support (thermodynamics, kinetics, properties prediction, spectroscopic data analysis) to the experimental efforts of the DOE Center of Excellence for Chemical Hydrogen Storage to reduce the time to design and develop new materials that meet the DOE targets.

- Focus on design of new materials and regeneration schemes.

• Experimental focus on organic and main group chemistries with better release and regeneration properties due to improved energy balance. Longer term alternatives.

Approach

- Use 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: the release and addition of H₂.
 - Use combination of validated molecular orbital theory and density functional theory
 - Key issues: Accuracy/reliability of models for real systems
- Develop new concepts to improve energy balance relevant for ease of H₂ release and regeneration of H₂ storage system.
- Develop new approaches to release hydrogen from organic and main group compounds based on new chemistries.
 - Demonstrate proof of concepts and key reactions.
- Key experimental issues:
 - Minimize weight by eliminating substituents or changing them into components that can store H_2 while maintaining kinetic and thermodynamic properties.
 - Demonstrating H₂ release reactions under expected operating conditions.
- Our team

Expt. Arduengo, Masaaki Yoshifuji (visiting faculty), Luigi Iconaru (grad student), Monica Vasiliu (grad student), Christian Schiel (postdoc),

Comp. Dixon, Myrna H. Matus (postdoc), Daniel Grant (grad student), Ted Grant (grad student), Monica Vasilu (grad student), Felix Fungo (REU undergrad), D.J. Outlaw (CBHP undergrad), Kevin Anderson (CBHP undergrad) Minh T. Nguyen (visiting faculty, Leuven)

Key Accomplishments

- Developed approach to predict heats of vaporization (liquid heats of formation) with new atomic parameters derived from experiment (CoE, LANL, R&H). 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 (CCSD(T)/CBS limit).

- Significant advances in reliable predictions of the thermodynamics of new H_2 chemical hydrogen storage systems to help groups focus experimental efforts. Example:

Calculated $C_x B_y N_z H_{12}$ (x+y+z = 6) chemistries – New aromatic compound $C_4 BNH_6$ (UO + UW & PNNL).

- 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 (CoE and U. Mo)

- Predicted kinetics for a range of H₂ release processes.
 - Extended work to alanes. Identified multiple transition states and new complexes. Interact with Metal Hydride CoE.
- Carbene experimental work completed. No go. Exploring different CBNH based on BH₃-imidazole structure computationally and new routes to AB.

Trapping of NH₂BH₂ by Ammonia Borane (AB)



Potential energy surfaces (kcal/mol) calculated at the G3MP2 and B3LYP/DZVP2 level

- **1.** H_2 elimination from AB *catalyzed* by NH_2BH_2 . Lowest energy paths lead to formation of two weakly interacting NH_2BH_2 molecules. (E[‡] = 27.0)
- **2.** Reaction of two NH_2BH_2 molecules to form the $BH_3NH_2BHNH_2$ chain. (E[‡] = 10.5)
- **3.** H_2 elimination from AB *catalyzed* by the $BH_3NH_2BHNH_2$ chain. (E[‡] = 30.3)

4. Chain elongation and cyclization to form the ring compound $B_2N_2H_7NH_2BH_3$ (NH₂BH₃ side chain bonded to B) resulting from addition of NH₂BH₂ to BH₃NH₂BHNH₂. (E[‡] = 9.8)



Only the isomer shown can be formed as observed because of the way the initial complexes in steps 2 and 4 form.

• Determined mechanism for H_2 elimination and showed initial polymer formation steps with specific regiochemistry. Done in collaboration with LANL experimental group.

G3MP2, B3LYP/DZVP2 gas phase enthalpies at 298 K. The accurate CCSD(T)/CBS (complete basis set) 6 result for the first step is -5.1 kcal/mol

C₄BN Ring Chemistry with S. Liu (Oregon)



Dehydrogenation Pathways and B-N BDE for the Aluminum Borane Amines





 Used computational predictions of energetics to improve process design and for process simulations

9



GOALS

- Obtain high yield in all steps.
- Avoid the formation of bonds that are too thermodynamically stable.
- Avoid formation of intermediates such as diborane (B₂H₆) to increase atom efficiency
- Recover and recycle all products
- Minimize the number of operations, especially separations.
- Provided benchmarked physical properties for process simulations such as boiling points, heats of formation, free energies, heat capacities

Enthalpies of Vaporization: Development of the Model



| Compound Name | BP _{calc} (K) | BP _{expt} (K) | ∆H _{vap, expt} kcal/mol | ΔS _{expt} e.u. | ΔH _{vap, calc} kcal/mol |
|---|------------------------|---------------------------|-------------------------------------|----------------------------|-------------------------------------|
| $H_2Sn(CH_3)_2$ | 292 | - | 6.8 | 23.3 | 6.7 |
| $Sn(C_4H_9)_4$ | 810 | - | 19.8 | 24.4 | 20.3 |
| $Sn(C_2H_5)_4$ | 474 | 454 | 12.2 | 25.8/26.9 | 11.8 |
| Sn(CH ₃) ₄ | 356 | 351 | 7.9 | 22.2/22.5 | 8.2 |
| Sn(C ₃ H ₇) ₄ | 634 | 501 | 16.0 | 25.2/31.9 | 15.8 |
| $Sn(CH_3)_3(C_2H_5)$ | 390 | - | 8.9 | 22.8 | 9.0 |
| HSn(CH ₃) ₃ | 326 | - | 7.2 | 22.2 | 7.5 |
| Sn(CH ₃) ₃ (t-Bu) | 424 | - | 12.9 | 30.5 | 10.6 |
| Ethanol | 355 | 351 | 10.0 | 28.2/28.5 | 8.9 |
| Diethylamine | 320 | 329 | 7.5 | 23.5/22.9 | 7.4 |
| C_6H_6 | 353 | 353 | 8.0 | 22.6/22.6 | 8.1 |
| PhSh | 431 | 442 | 11.4 | 26.4/25.8 | 10.8 |
| 1,2Ph(SH) ₂ | 518 | 512 | | | 13.0 |

- Combi2005 parameters with Nring parameter plus new dispersion parameters for B, AI, Sn, S
- Experimental data from CRC Handbook, *NIST*, Pedley, or Cox and Wagman
- $\Delta H_{vap} = \Delta S_{vap} T_{BP}$. Pictet and Trouton empirically showed $\Delta S \sim 22 \text{ e.u.} \Delta S_{vap}$. $\Delta S_{vap} = 25 \text{ e.u.}, \Delta S_{vap} = 22 \text{ e.u.}$.
- Developed validated, new approach with new atomic parameters to predict T_{BP} , ΔH_{vap} , $\Delta H(liquid)$ for reactor and separations design. Uses accurate calculated $\Delta H(gas)$. Data 11 used in process simulations.

Examples of Thermodynamic Properties for Process Simulation Modeling



| Compound Name | BP _{cosmo-RS} | $\Delta H_{vap, 0.023}$ | $\Delta H_{vap, 0.025}$ | C _v |
|--|------------------------|-------------------------|-------------------------|----------------|
| | K | kcal/mol | kcal/mol | cal/mol-K |
| AI(OCH ₃) ₃ | 487.1 | 11.2 | 12.2 | 33.8 |
| (1,2-C ₆ H ₄ S ₂)BHNH ₃ | 854.8 | 19.7 | 21.4 | 36.9 |
| $HSn(C_4H_9)_3$ | 676.9 | 15.6 | 16.9 | 70.0 |
| 1,2-C ₆ H ₄ (SH)(SSn(C ₄ H ₉) ₃) | 1029.2 | 23.7 | 25.7 | 102.4 |
| $H_2Sn(C_4H_9)_2$ | 521.0 | 12.0 | 13.0 | 51.2 |
| $(1,2-C_6H_4S_2)Sn(C_4H_9)_2$ | 894.3 | 20.6 | 22.4 | 76.8 |
| $NH_3BH(SC_6H_5)_2$ | 1017.7 | 23.4 | 25.4 | 59.7 |
| $(1,2-C_6H_4(SSn(C_4H_9)_3)_2)$ | 1505.7 | 34.6 | 37.6 | 175.5 |
| (1,2-C ₆ H ₄ S ₂)BHNH(C ₂ H ₅) ₂ | 871.8 | 20.1 | 21.8 | 56.2 |
| $CH_3NH_2BH_3$ | 586.7 | 13.5 | 14.7 | 16.2 |
| $B_3N_3H_3(CH_3)_3$ | 668.7 | 15.4 | 16.7 | 42.9 |
| $BH_3NH(C_2H_5)_2$ | 557.2 | 12.8 | 13.9 | 31.0 |

• Used new approach to predict thermodynamic data for direct use in process simulations.

- Experimental feedback in terms of compounds to study, $T_{\rm BP}\!$, fit to process simulation data.

Thermo for LANL AB Regeneration Pathway

| Reactor 1: | | $\Delta H(kcal/mol)$ |
|-----------------|--|----------------------|
| Digestion | (1a) BNH + 1.5 $C_6H_4(SH)_2 \rightarrow 0.5 HB(C_6H_4S_2) \cdot NH_3 + 0.5 (NH_4)B(C_6H_4S_2)_2$ | 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 ₆ H ₄ S ₂) ₂ + 0.5 Bu ₃ SnH → 0.5 HB(C ₆ H ₄ S ₂)·NH ₃ + 0.5 (C ₆ H 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 ₆ H4S ₂)·NH ₃ + 0.5 (NH ₄)B(C ₆ H ₄ S ₂) ₂ + Et ₂ NH + 2.5 Bu ₃ SnH | 4 |
| | \rightarrow Et ₂ NHBH ₃ + NH ₃ + 0.5 (C ₆ H ₄)(SH)(SSnBu ₃) + C ₆ H 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) $Et_2NHBH_3 + NH_3(I) \leftrightarrows H_3NBH_3 + Et_2NH$ | -7.3 |
| Reactor 4: | | |
| Metal Recycle: | (4a) $C_6H_4(SSnBu_3)_2 + 2H_2 \rightarrow C_6H_4(SH)_2 + 2Bu_3SnH$ | 18.7 |
| - | (4b) $0.5 C_6 H_4(SH)(SSnBu_3) + 0.5 H_2 \rightarrow 0.5 C_6 H_4(SH)_2 + 0.5 Bu_3SnH$ | 6.8 |
| | | |



Los Alamos

ROHM

13

Assess Thermodynamic Efficiency of 1st Fill

| Metal Regeneration Scheme | ΔH |
|---|--------|
| $NH_4B(OMe)_4 (s) + NH_4CI (s) + LiAIH_4 (s) \rightarrow$ $NH_6BH_6 (s) + AI(OMe)_6 (l) + MeOH (l) + H_6 (a) + LiCI (s) + NH_6 (a)$ | -65 4 |
| NaCl (s) + electricity \rightarrow Na (s) + $\frac{1}{2}$ Cl ₂ (g) | 98.2 |
| $\frac{1}{2} Cl_2(g) + \frac{1}{2} H_2(g) \rightarrow HCl(g)$ | -22.1 |
| HCl (g) + NH ₃ (g) \rightarrow NH ₄ Cl (s) | -42.1 |
| $AI(OMe)_3 (I) + 3/2 H_2 (g) + electricity \rightarrow AI (s) + 3 MeOH (I)$ | 48.0 |
| Na (s) + Al (s) + 2 $H_2(g) \rightarrow NaAlH_4(s)$ | -27.6 |
| LiCl (s) + NaAlH ₄ (s) \rightarrow LiAlH ₄ (s) + NaCl (s) | 2.4 |
| Overall reaction: $NH_4B(OMe)_4$ (s) + 3 H_2 (g) $\rightarrow NH_3BH_3$ (s) + 4 | |
| MeOH (I) | -8.6 |
| Sum of exothermicities | -157.2 |
| Sum of endothermicities | 148.6 |
| Efficiency with 0% heat recovery | 46% |
| Efficiency with 20% heat recovery | 50% |

Thermodynamics is best one can do with perfect separations and process efficiencies

Ramachandran, P. V.; Gagare, P. D. Inorg. Chem. 2007, 46, 7810-7817.

Reaction Thermodynamics to Release BH₃NH₃

| М | R | ΔΗ | ΔG |
|----|----------------------------------|-------|-------|
| Sn | CH ₃ | 3.8 | 12.5 |
| Ge | CH ₃ | 9.4 | 19.0 |
| Si | CH ₃ | 9.2 | 20.1 |
| In | CH ₃ | -35.2 | -21.2 |
| Ga | CH ₃ | -31.6 | -17.2 |
| AI | CH ₃ | -44.3 | -30.6 |
| Sn | C_6H_5 | 5.8 | 15.6 |
| Ge | C_6H_5 | 11.3 | 24.0 |
| Si | C_6H_5 | 11.0 | 24.5 |
| In | C_6H_5 | -27.2 | -13.8 |
| Ga | C_6H_5 | -22.2 | -9.5 |
| AI | C_6H_5 | -36.0 | -22.2 |
| Sn | $c-C_6H_{11}$ | 3.0 | 10.5 |
| Ge | $c-C_6H_{11}$ | -0.6 | 12.6 |
| Si | c-C ₆ H ₁₁ | 14.0 | 26.0 |
| In | $c-C_6H_{11}$ | -37.4 | -20.7 |
| Ga | $c-C_6H_{11}$ | -30.5 | -18.7 |
| AI | c-C ₆ H ₁₁ | -43.6 | -27.8 |



| Μ | R | ΔΗ | ΔG |
|----|---------------------------------|-------|-------|
| Sn | n-C ₄ H ₉ | 3.5 | 12.8 |
| Ge | n-C ₄ H ₉ | 9.8 | 21.8 |
| Si | n-C ₄ H ₉ | 10.9 | 24.1 |
| In | n-C ₄ H ₉ | -35.2 | -22.1 |
| Ga | n-C ₄ H ₉ | -31.1 | -17.0 |
| Al | n-C ₄ H ₉ | -44.1 | -28.9 |
| Sn | t-C ₄ H ₉ | 6.7 | 18.3 |
| Ge | t-C ₄ H ₉ | 20.3 | 33.0 |
| Si | $t-C_4H_9$ | 26.1 | 40.0 |
| In | t-C ₄ H ₉ | -23.0 | -11.9 |
| Ga | t-C ₄ H ₉ | -18.7 | -7.3 |
| Al | $t-C_4H_9$ | -91.8 | -78.6 |

• Searched for lower mass reducing agent (Pb also studied). Showed that Group IIIA elements have potential with good thermodynamics. Predict optimal substituents for experiment.

• Discoveredd potential reducing agent reactions to eliminate amine exchange/recycle step

Reaction Thermodynamics to Eliminate CO₂ Recycle

| | | R | R' | ΔΗ | ΔG | R | R |
|--|-------------------------------|-----------------|----------------------------------|------|----------|---------------------------------|----|
| | $(R,M)(R')NC(O)H \rightarrow$ | Н | Н | 17.9 | 8.3 | n-C ₄ H ₉ | Н |
| | | CH ₃ | Н | 19.2 | 9.5 | $n-C_4H_9$ | С |
| | HMR ₃ + (R')N=C=O | CH_3 | CH ₃ | 17.9 | 5.2 | $n-C_4H_9$ | n- |
| | M = Sn | CH_3 | n-C ₄ H ₉ | 16.3 | 4.1 | $n-C_4H_9$ | t- |
| | | CH_3 | t-C ₄ H ₉ | 10.1 | -5.2 | $n-C_4H_9$ | n- |
| | Reaction Energies at | CH_3 | $n-C_6H_{13}$ | 16.1 | 4.1 | $n-C_4H_9$ | C- |
| | (Sn)/DZVP2 (H, C, N, | CH ₃ | c-C ₆ H ₁₁ | 7.9 | -4.7 | $n-C_4H_9$ | С |
| | O) Level at 298 K in | CH_3 | C_6H_5 | 14.1 | 2.2 | $n-C_4H_9$ | С |
| | KCal/mol. | CH_3 | C_6H_4CI | 14.8 | 2.7 | $n-C_4H_9$ | С |
| | | CH_3 | $C_6H_4NO_2$ | 16.3 | 4.1 | C_6H_5 | Н |
| Predicted best substitutents R and R' to | C_2H_5 | Н | 20.0 | 11.0 | C_6H_5 | С | |
| | aet optimal | C_2H_5 | CH_3 | 18.4 | 6.8 | C_6H_5 | n |
| | thermodyanmics | C_2H_5 | $n-C_4H_9$ | 17.0 | 5.6 | C_6H_5 | t- |
| | • Showed that R = | C_2H_5 | $t-C_4H_9$ | 10.1 | -3.6 | C_6H_5 | n |
| | phenyl may be a useful | C_2H_5 | $n-C_6H_{13}$ | 16.8 | 5.7 | C_6H_5 | C- |
| | Improved reaction | C_2H_5 | c-C ₆ H ₁₁ | 8.8 | -3.9 | C_6H_5 | С |
| | design for isocyanate | C_2H_5 | C_6H_5 | 15.1 | 2.9 | C_6H_5 | С |
| | chemistry | C_2H_5 | C_6H_4CI | 16.0 | 4.1 | C_6H_5 | С |
| | | C_2H_5 | $C_6H_4NO_2$ | 17.6 | 5.7 | | |

| R | R′ | ΔH | ΔG |
|---------------------------------|----------------------------------|------|------|
| n-C ₄ H ₉ | Н | 17.5 | 7.1 |
| n-C ₄ H ₉ | CH_3 | 19.1 | 6.2 |
| n-C ₄ H ₉ | $n-C_4H_9$ | 17.1 | 6.1 |
| n-C ₄ H ₉ | $t-C_4H_9$ | 10.2 | -3.6 |
| n-C ₄ H ₉ | $n-C_6H_{13}$ | 17.0 | 4.8 |
| n-C ₄ H ₉ | c-C ₆ H ₁₁ | 8.9 | -2.6 |
| n-C ₄ H ₉ | C_6H_5 | 15.4 | 4.1 |
| n-C ₄ H ₉ | C ₆ H ₄ Cl | 16.3 | 5.5 |
| n-C ₄ H ₉ | $C_6H_4NO_2$ | 18.1 | 7.1 |
| C_6H_5 | Н | 19.1 | 7.1 |
| C_6H_5 | CH_3 | 17.9 | 3.3 |
| C_6H_5 | n-C ₄ H ₉ | 16.4 | 2.9 |
| C_6H_5 | $t-C_4H_9$ | 8.5 | -6.9 |
| C_6H_5 | $n-C_6H_{13}$ | 16.1 | 2.4 |
| C_6H_5 | $c-C_6H_{11}$ | 7.2 | -6.0 |
| C_6H_5 | C_6H_5 | 13.2 | -0.3 |
| C_6H_5 | C_6H_4CI | 14.2 | 0.6 |
| C_6H_5 | $C_6H_4NO_2$ | 16.0 | 2.3 |
| | | | |

Synthesis of AB: Borane Transfer Technology



- A borane transfer process has been developed based on a du Pont Patent (No. 5,034,464; A.J. Arduengo, July 23, 1991))
- New process facilitates transfer of a BH₃ unit from sodium borohydride to a variety of amines (including ammonia) with the intermediacy of a proprietary borane transfer agent.
 Overall yield in early experiments is 80 95%.

A Novel Hydrogen Activation Process

• 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.



• Established that the interaction of H_2 with the electrophile is a key step in the activation process.

• Electrophiles to replace the $Fe(CO)_5$ such as **BBr**₃, B(OCH₃)₃, 1-bora-adamantane, and **trityl cation** reacting with an imidazolylidene nucleophile have been investigated. **Crimson** compounds work.

• Provided another way to make H₂ into a proton and hydride (like BH₃NH₃) or PNNL work for regeneration cycles.



Imidazolium acylferrate formed in the absence of H₂ (either at -78 °C or RT).
In the presence of H₂ at -78 °C,

obtained the imidazolium hydridoferrate salt formed (hydrogen fixation).

• The scope and utility of the reaction especially for regeneration is being investigated

• Experiments with a partner in Bonn, Germany will allow the study of the reaction in a low temperature atuoclave. 18

Collaborations

The UA team is involved in extensive collaborations with Center partners as outlined in the presentation especially in the use of computational chemistry to support Center goals. The UA computational effort is fully integrated with the Center partners.

Examples:

External computational collaborations

- Energetics for AB compounds: LANL, PNNL, Penn
- Release and regeneration mechanisms: LANL, PNNL, Penn, UC-Davis, UW
- Polymerization mechanisms: LANL, PNNL, Penn
- Catalyst design: CoE
- Spectroscopic predictions: CoE
- Boron hydride anions: U. Missouri
- Nanoparticles & main group chemistry: UC-Davis
- C_xB_yN_zH₁₂ thermodynamics: UW & new CoE collaborators
- (E(NH₂BH₃)_m thermodynamics & kinetics: U. Mo. & new CoE collaborators

Experimental collaborations

Organic/main group chemistry: LANL

Future Work

Continue to use computational chemistry to support overall center efforts in H₂ release, AB regeneration, new storage concepts including alternative inorganic and organic compounds and reaction mechanisms.

- Use density functional theory (DFT) benchmarked by accurate methods.

- Calculate thermodynamics, molecular properties for engineering simulations, and kinetics.

- Test new molecular properties against available experimental data. Improve parameterization schemes.

- Predict reaction mechanisms and efficiencies.

- Computational design of new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metal catalysts for release and regeneration.
- Regeneration mechanisms. Predict energetics and kinetics of key steps (examples: digestion, reduction, etc.) to optimize experimental approach.
- Ammonia borane chemistry new metal/main group BNH compounds (E(NH₂BH₃)_m. Solid state chemistry and reaction products. What is formed?
- Further studies of CBNH_x mechanisms.
- Predict spectroscopic properties (nmr, IR/Raman, UV-vis) for use in analyzing experimental data.
- Improve % H₂ release kinetics by using Amino(*Imidazolo*)-Boranes.
- Develop new route to synthesis of AB for 1st fill.

Amino(Imidazolo)-Boranes to improve H₂ activation



- Study hydrogen elimination from azolium borohydrides (polymeric amine borane analogs).
- Expand to include 1,2,4-triazoles and tetrazole.
- Reduced basicity of heterocyclic systems containing multiple nitrogens is such that amineborane 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.

• In the next period, obtain stable azole-borane adducts by starting from the more basic azolides (azole-anions).

UA Summary

• Relevance: Develop new materials for chemical H₂ storage to meet DOE needs. Address issues of System Cost, System Weight and Volume, and Spent Fuel Regeneration.

• Approach: Develop promising approaches to chemical H₂ storage for current and future DOE targets using computational chemistry and synthetic organic/inorganic chemistry

• Technical Accomplishments: Significant advances in predicting the thermodynamics of new H₂ chemical hydrogen storage systems and for a broad range of regeneration mechanisms. Developed new approach for predicting thermodynamic properties for process simulations. New alane chemistries. Synthesized imidazole borane adduct that readily releases hydrogen at room temperature.

• Collaborations: Provide computational chemistry support for the DOE Center of Excellence in Chemical Hydrogen Storage. Interact with all partners. Interact closely with LANL on organic chemistry synthetic strategies.

• Future Research: Use computational chemistry to support overall Center efforts in H_2 release, spent fuel regeneration, new concepts including alternative inorganic and organic compounds, and mechanisms for H_2 release and regeneration. Improve % H_2 by mass stored and kinetics for H_2 release for main group substituted organic 22 compounds.

UA Summary Table

| Storage Parameter: DOE 2010 System Targets | Carbene/Cyanocarbon | Imidazolo Borane |
|--|--|--|
| Material Gravimetric Capacity: 6 wt% | Current: 2% Ultimate for C ₂ N ₂ H ₆ polymer: 10.3% | Current: 1% Ultimate: 7.1% |
| Material Volumetric Capacity: 0.045 kg/L | Current: 0.045 Ultimate: 0.098 | Current: ~0.02 Ultimate: 0.098 |
| Dehydrogenation Rate 0.02g/s-kW | In progress for polymer | Rate of H ₂ release: 9.6 ± 0.5 M ⁻¹ s ⁻¹ |
| Storage Efficiency Center Goal: 50% Near thermoneutral | Exothermic: -5 kcal/mol Ultimate: Thermoneutral | In progress |

Supplemental Slides

Schematic energy profiles for H₂release in alane ammonia systems. Relative energies in kcal/mol from CCSD(T)/aVTZ + ZPE calculations.

Two $AIH_3 + 2NH_3$



Dehydrogenation Pathways and B-N BDEs for the Phosphorus Amine Boranes



Reaction Thermodynamics to Eliminate CO₂ Recycle



Predict energetics for alternative approaches to eliminate CO₂ recycle. Help to identify optimal paths.
Conformational flexibility and steric crowding are issues which we are addressing in the calculations.

Reaction Thermodynamics to Eliminate CO₂ Recycle

Reaction Energies Calculated at the B3LYP/VDZ-PP (Sn)/DZVP2 (H, C, N, O) at 298 K in kcal/mol.

Formate and inorganic acid reactions (LANL & Penn) – Sn by-products

| Reaction | ΔΗ | ΔG |
|--|-------|-------|
| $Bu_3Sn-SC_6H_5 + H-CI> Bu_3Sn-CI + H-SC_6H_5$ | -11.0 | -14.6 |
| Bu ₃ Sn-SC ₆ H ₅ + H-Br> Bu ₃ Sn-Br + H-SC ₆ H ₅ | -14.3 | -17.0 |
| Bu ₃ Sn-SC ₆ H ₅ + HC=O(OH)> Bu ₃ Sn-OOCH + H-SC ₆ H ₅ | 1.3 | -1.6 |
| Bu ₃ Sn-Cl + HCOOH> Bu ₃ Sn-OOCH + HCl | 12.4 | 13.0 |
| Bu ₃ Sn-Br + HCOOH> Bu ₃ Sn-OOCH + HBr | 15.6 | 15.4 |
| $C_6H_4(SH)(SSnBu_3) + HCOOH> C_6H_4(SH)_2 + HCOO-SnBu_3$ | 2.4 | 1.1 |

Isocyanates as an alternative to formate/CO₂ chemistry

| R | R' | ΔΗ | ΔG |
|----------------------------------|-----------------|------|------|
| Н | CH ₃ | 12.0 | 12.8 |
| CH ₃ | CH_3 | 11.2 | 12.3 |
| C_6H_5 | CH_3 | 15.2 | 16.7 |
| c-C ₆ H ₁₁ | CH_3 | 13.8 | 15.0 |
| n-C ₄ H ₉ | CH_3 | 12.0 | 13.2 |
| t-C ₄ H ₉ | CH_3 | 13.8 | 16.0 |
| Н | C_6H_5 | 11.9 | 13.2 |
| CH ₃ | C_6H_5 | 11.8 | 11.4 |
| C_6H_5 | C_6H_5 | 15.2 | 16.4 |

$(R'_3)SnS-R + RHNC(O)H \rightarrow (R'_3)Sn-RNC(O)H + HSR$

• Predicted reaction thermodynamics for formate and inorganic reactions for regneration.

• Predicted best set of substitutents for Sn-S isocyanate chemistry.