Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

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DOE Center of Excellence for Chemical Hydrogen Storage
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This presentation does not contain any proprietary or confidential information
Overview

Timeline

• Project start date: Jan. 05
• Project end date: FY10
• Percent complete: 40%

Barriers

DOE Barriers addressed
– Cost
– Weight and Volume
– Efficiency
– Regeneration

Budget

• Projected total project funding: $1,780,690
  – DOE share: $1,273,711 (requested)
  – UA share: $506,979
• Funding for FY05: $431K
  $225K (DOE), $206K (UA)
• Funding for FY06: $430K
  $300K (DOE), $130K (UA)

Partners

DOE Center of Excellence for Chemical Hydrogen Storage: with LANL, PNNL UW, UC-Davis, Penn State, UA, UPenn, Northern Arizona, UCLA a Millenium Cell, Rohm and Haas, and US Borax.
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 H₂ activation chemistry

• Develop and implement systems based on polyhydrides of main group elements: phosphorus, boron, nitrogen

• Develop and implement cyanocarbon systems for H₂ 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.
Approach

• Use novel chemistry approaches to synthesize compounds for easily reversible addition/elimination of H₂ based on our novel, stable carbene chemistry for use in H₂ storage systems.

• Develop new synthetic approaches to use organo-nitrogen compounds for hydrogen storage. Potential weight savings by using storage media as structural material.

• Use 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 H₂.

• Develop thermodynamic approach for chemical H₂ storage based on exploiting ΔH and ΔG coupled with Le Chatelier’s principle to manage H₂ addition and release in chemical compounds. Potential solution for cold-start issues and regeneration. Develop kinetic models for hydrogen storage, release, and material regeneration.
Partnerships/Collaborations

- Los Alamos National Laboratory (LANL)
  - Coordinate on the design, synthesis and characterization of new organic compounds with higher H₂ storage capability
  - Computational chemistry predictions for borane-amine chemistry
  - Computational chemistry predictions of regeneration reaction pathways

Pacific Northwest National Laboratory (PNNL)
  - Computational chemistry predictions for borane-amine chemistry

Penn State University and the University of Pennsylvania
  - Computational chemistry predictions for borane-amine chemistry and prediction of nmr chemical shifts

University of California – Los Angeles
  - Computational chemistry predictions of borane chemistry – heats of formation

University of California – Davis
  - Computational chemistry predictions of boron/silicon bond energies
UA Experimental Technical Accomplishments

- **Carbenes**
  - Structural characterization of an imidazolium borohydride.
  - Formation of carbene·H₂ adducts.
  - Carbenium ions isolated in both reduced (hydrogen storage) and oxidized (hydrogen released forms).
  - Polycarbene architecture synthesized.

- **Cyanocarbons**
  - Model compound available for cyanocarbon·H₂ adducts.
  - New pyridazine hydrogen storage candidate isolated.
  - **Phosphocarbons**
  - Room temperature (uncatalyzed) hydrogen uptake achieved.
Borane-amine mechanisms
- First reliable predictions of the energetics of borane amine molecules
- Developed model of the chemical bonds and bond energies in borane amines
- First predictions of borane amine reaction dehydrogenation kinetics
- Identified bridging intermediate in borane-amine polymerization mechanism based on calculated nmr chemical shifts
- Studied isoelectronic compounds
- Full configuration interaction calculations on states of diatomics
- Predicted heats of formation of borane amine salts including $\text{B}_{12}\text{H}_{12}{\text{2}}^{\text{2}}(\text{NH}_4^+)_2$

Borane-amine regeneration chemistry
- First predictions of energetics for regeneration reactions

Carbene and cyanocarbon chemistry
- First reliable predictions of the energetics of carbenes. Discovered new scale for defining carbene reactivity
- First reliable predictions of the energetics of model nitrogen based compounds. Discovered important effect of organic substituents in making H$_2$ release energetics more favorable.

BH/SiH bond energies
- First reliable predictions of the bond energies in B/Si compounds
Heteroatom Organic Systems for Hydrogen Storage: The “Alabama Approach”

Developed new approaches to release hydrogen from dihydroimidazoles, based on new chemistry and our world leadership in stable carbene chemistry.

1,5 elimination to give fused diimidazolium rings:

- Hydrogen elimination is symmetric (non-polar (*) )
- No metal catalyst required (substituents on N, C)
- Endothermic dehydrogenation, $P_{eq} < 1$ atm

1,1 elimination to give carbene products:

- Hydrogen elimination is symmetric (non-polar (*) )
- Metal catalyst required (substituents on N, C)
- Endothermic dehydrogenation, $P_{eq} < 1$ atm
Developed new chemistry concept to increase capacity

- Fusing 3 dihydroimidazole rings into "propellane" structure:
  - Lightest possible material is $\text{C}_5\text{H}_{12}\text{N}_6$, forming $\text{C}_5\text{H}_6\text{N}_6 + 3 \text{H}_2$ (3.9 wt %)
  - Reaction currently under study for N-substituted analogs

Ultimate goal:

- Lateral condensation with \(-\text{CH}_2\)- links
  - gives material $\text{C}_8\text{H}_{12}\text{N}_6$, forming $\text{C}_8\text{N}_6 + 6 \text{H}_2$ (6.3 wt %)
  - Routes to such materials under study;
    - one possible precursor is the urea compound
  - Designed poly-carbene product
Carbenes for H₂ Storage Systems

Showed that carbon-based systems exist that have more accessible CH bonds than traditional hydrocarbons: \( C₂H₆ \rightarrow C₂H₄ + H₂ \quad \Delta H(298) = 32.6 \text{ kcal/mol} \)

Based on Arduengo’s stable carbene
Carbene Reaction Energetics for H₂ storage at 298K in kcal/mol to ± 1 kcal/mol

\[
\text{carbene + } H_2 \rightarrow \text{carbeneH}_2 \quad \Delta H = -14.9
\]
Adding H₂ to the carbene is exothermic by 14.9 kcal/mol -- very nice in managing release because we can use \( \Delta G \) to pull it off using Le Chatelier’s Principle. \( T\Delta S(298K) = +8.2 \) kcal/mol

\[
\text{carbene} + H^{+} \rightarrow \text{carbeneH}^{+} \quad \Delta H = -249.5
\]
The PA of the simplest carbene is 249.1 kcal/mol. Very basic!

\[
\text{carbene} \rightarrow {}^3\text{carbene} \quad \Delta H = 90.5
\]
The singlet triplet splitting of the carbene is very large!

\[
\text{carbene} + H \rightarrow \text{carbeneH} \quad \Delta H = -31.8
\]
The C-H bond energy for adding an H to the carbene shows a weak C-H bond.

\[
\text{carbeneH} + e^- \rightarrow \text{carbeneH}^- \quad \Delta H = 5.0
\]
Addition of H- to the simplest carbene leads to autodetachment of the e⁻.

\[
\text{Carbene} + H_2 \rightarrow \text{carbeneH}_6 \quad \Delta H = -8.6
\]
Adding H₂ to hydrogenate the double bond is exothermic by only 9 kcal/mol as compared to -31 kcal/mol for hydrogenation of C₂H₄.

\[
\text{CarbeneH}_6 + H_2 \rightarrow \text{carbeneH}_8 \quad \Delta H = -32.6
\]
Adding H₂ to the hydrogenated carbene is quite exothermic – develop carbene reactivity scale.

11
First Synthesis of Tris(carbene)
Interconversion of Tricyclics and First Synthesis of Fused Diimidazolium rings for 1,5 Hydrogen Elimination Reactions
Another Approach to Fused Diimidazolium rings for 1,5 Hydrogen Elimination Reactions

Carbenium ion storage candidates isolated and characterized. Both forms (oxidized and reduced) are available.
First Crystal Structures of Bis(imidazolium) Ions

9

10

[Ox] (-H₂)  [Red] (+H₂)

2 BF₄⁻
Cyanocarbons for Hydrogen Storage

Developed new concept to increase capacity and minimize weight by providing structural benefits

Materials prepared having both hydrazine and triazine moieties:

Ultimate goal:

- Polymers based on these moieties, idealized composition $C_3H_9N_6 \rightarrow C_3N_6 + 4.5 \text{ H}_2$ (7.0 wt % $\text{H}_2$)

- Combines both hexahydrotriazine $\rightarrow$ triazine, and hydrazo $\rightarrow$ diaza dehydrogenation concepts, expected to be more robust than unsubstituted hexahydrotriazine

- Expect will have similar needs for effective hydrogenation/dehydrogenation catalysts as hexahydrotriazine
Cyanocarbon chemistry

• Can we use derivatives of cyanocarbons for chemical H$_2$ storage systems?
  Similar to melamine chemistry so we can generate stable structural components.

• Predicted reaction energies (kcal/mol) due to limited available data.

• Simplest model is conversion of N=N bonds to N-N bonds
  \[ N_2 + H_2 \rightarrow N_2H_2 \quad \Delta H = 48.2 \]
  \[ N_2H_2 + H_2 \rightarrow N_2H_4 \quad \Delta H = -25.1 \]
  \[ N_2H_4 + H_2 \rightarrow 2NH_3 \quad \Delta H = -43.0 \]

• Substitution of an organic group for the H can dramatically change the energetics making favorable materials for H$_2$ release
  \[ (CH_3)HNNH(CH_3) \rightarrow (CH_3)N=N(CH_3) + H_2 \quad \Delta H (298 \text{ K}) = -13.8 \]
  \[ \Delta G (298 \text{ K}) = -5.1 \]

Work to be done
  • Predict reaction energies for more complex systems
  • Design appropriate catalysts
  • Structural properties - geometric effects (polymer vs model compounds)
  • Effects of conjugation,
  • Ease of reduction/oxidation
  • Polymer synthesis
Cyanocarbon·$\text{H}_2$ Adduct Synthesis

Theoretical models suggest that molecular re-orientation has to be controlled to manage hydrogen uptake and release. The issue is being studied experimentally.
Pyridazine Solution to Conjugation: An approach to deal with the re-orientation issue

A new pyridazine compound was synthesized to provide a back-up position for the re-orientation problem.
Hydrogen Production Using Ammonia-Borane

\[ [-\text{H}_2\text{N-BH}_2^-]_n \xrightarrow{-\text{H}_2} \text{Linear polymer} \]

\[ \text{H}_3\text{N-BH}_3 \xrightarrow{-3\text{H}_2} \text{BN} \]

\[ \text{Cyclic trimer} \quad \text{‘borazane’} \]

\[ \text{Cyclic trimer} \quad \text{‘borazine’} \]

\[ \text{‘diamondoid’} \]

\[ \text{‘graphitic’} \]

Collaborators: Fran Stephens & Tom Baker, LANL
### Energetics (kcal/mol) for the Release of H₂ (Gas Phase Model)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (298K)</th>
<th>TS Energy</th>
<th>Bond Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH₃NH₃ → BH₂NH₂ + H₂</td>
<td>-8.3</td>
<td>34.5</td>
<td>25.9</td>
</tr>
<tr>
<td>BH₂NH₂ → HBNH + H₂</td>
<td>31.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HBNH → BN + H₂</td>
<td>134.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlH₃NH₃ → AlH₂NH₂ + H₂</td>
<td>5.0</td>
<td>27.6</td>
<td>26.1</td>
</tr>
<tr>
<td>AlH₂NH₂ → HAINH + H₂</td>
<td>61.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlHNH → AlN + H₂</td>
<td>74.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH₃PH₃ → BH₂PH₂ + H₂</td>
<td>17.4</td>
<td>30.4</td>
<td>21.1</td>
</tr>
<tr>
<td>BH₂PH₂ → HBPH + H₂</td>
<td>31.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHPH → BP + H₂</td>
<td>82.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlH₃PH₃ → AlH₂PH₂ + H₂</td>
<td>5.6</td>
<td>34.4</td>
<td>14.0</td>
</tr>
<tr>
<td>AlH₂PH₂ → HAlPH + H₂</td>
<td>34.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlHPH → AlP + H₂</td>
<td>45.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BH₄⁻][NH₄⁺] (s) → BH₃NH₃(g) + H₂</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BH₄⁻][PH₄⁺] (s) → BH₃PH₃ + H₂</td>
<td>-13.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[AlH₄⁻][NH₄⁺] (s) → AlH₃NH₃ + H₂</td>
<td>-3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[AlH₄⁻][PH₄⁺] (s) → AlH₃PH₃ + H₂</td>
<td>-9.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Isoelectronic species – no obvious advantage energetically and less capacity due to mass.
- Direct H₂ elimination above dative bond energy (consistent with experiment) – need catalysts.
Predicted cyclization reaction energetics in the gas phase in kcal/mol

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (298K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Highly accurate CCSD(T)/CBS</strong></td>
<td></td>
</tr>
<tr>
<td>$3\text{BH}_3\text{NH}_3 \rightarrow \text{c-(BH}_2\text{NH}_2)_3 + 3\text{H}_2$</td>
<td>-54.5</td>
</tr>
<tr>
<td>$\text{c-(BH}_2\text{NH}_2)_3 \rightarrow \text{c-(BHNH)}_3 + 3\text{H}_2$</td>
<td>-20.4</td>
</tr>
<tr>
<td><strong>G3MP2</strong></td>
<td></td>
</tr>
<tr>
<td>$3\text{BH}_3\text{NH}_3 \rightarrow \text{c-(BH}_2\text{NH}_2)_3 + 3\text{H}_2$</td>
<td>-60.8</td>
</tr>
<tr>
<td>$\text{c-(BH}_2\text{NH}_2)_3 \rightarrow \text{c-(BHNH)}_3 + 3\text{H}_2$</td>
<td>-23.4</td>
</tr>
<tr>
<td>$3\text{BH}_3\text{PH}_3 \rightarrow \text{c-(BH}_2\text{PH}_2)_3 + 3\text{H}_2$</td>
<td>-49.1</td>
</tr>
<tr>
<td>$\text{c-(BH}_2\text{PH}_2)_3 \rightarrow \text{c-(BHPH)}_3 + 3\text{H}_2$</td>
<td>57.0</td>
</tr>
<tr>
<td>$3\text{AlH}_3\text{NH}_3 \rightarrow \text{c-(AlH}_2\text{NH}_2)_3 + 3\text{H}_2$</td>
<td>-83.6</td>
</tr>
<tr>
<td>$\text{c-(AlH}_2\text{NH}_2)_3 \rightarrow \text{c-(AlHNH)}_3 + 3\text{H}_2$</td>
<td>25.1</td>
</tr>
<tr>
<td>$3\text{AlH}_3\text{PH}_3 \rightarrow \text{c-(AlH}_2\text{PH}_2)_3 + 3\text{H}_2$</td>
<td>-64.7</td>
</tr>
<tr>
<td>$\text{c-(AlH}_2\text{PH}_2)_3 \rightarrow \text{c-(AlHPH)}_3 + 3\text{H}_2$</td>
<td>17.2</td>
</tr>
</tbody>
</table>

- Very exothermic processes in the gas phase. Need to investigate condensed phase energetics.
- Key issues are the heat of fusion and vaporization of BH$_3$NH$_3$ and the associated intermolecular interactions.
BN Cyclization reaction energetics in kcal/mol

Formation of boron-nitrogen cycles, \((\text{BH}_2\text{NH}_2)_n\), for \(n = 2\) to \(7\), \(9\) and \(13\), 
\(\text{(B3LYP/DGDZVP2 at 0K)}\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta E)</th>
<th>(\Delta E/n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\text{BH}_3\text{NH}_3 \rightarrow \text{c-}(\text{BH}_2\text{NH}_2)_2 + 2\text{H}_2)</td>
<td>-26.9</td>
<td>-13.4</td>
</tr>
<tr>
<td>(3\text{BH}_3\text{NH}_3 \rightarrow \text{c-}(\text{BH}_2\text{NH}_2)_3 + 3\text{H}_2)</td>
<td>-52.3</td>
<td>-14.5</td>
</tr>
<tr>
<td>(4\text{BH}_3\text{NH}_3 \rightarrow \text{c-}(\text{BH}_2\text{NH}_2)_4 + 4\text{H}_2)</td>
<td>-64.6</td>
<td>-16.2</td>
</tr>
<tr>
<td>(5\text{BH}_3\text{NH}_3 \rightarrow \text{c-}(\text{BH}_2\text{NH}_2)_5 + 5\text{H}_2)</td>
<td>-78.2</td>
<td>-15.6</td>
</tr>
<tr>
<td>(6\text{BH}_3\text{NH}_3 \rightarrow \text{c-}(\text{BH}_2\text{NH}_2)_6 + 6\text{H}_2)</td>
<td>-94.1</td>
<td>-15.7</td>
</tr>
<tr>
<td>(7\text{BH}_3\text{NH}_3 \rightarrow \text{c-}(\text{BH}_2\text{NH}_2)_7 + 7\text{H}_2)</td>
<td>-113.9</td>
<td>-16.3</td>
</tr>
<tr>
<td>(9\text{BH}_3\text{NH}_3 \rightarrow \text{c-}(\text{BH}_2\text{NH}_2)_9 + 9\text{H}_2)</td>
<td>-144.0</td>
<td>-16.0</td>
</tr>
<tr>
<td>(13\text{BH}_3\text{NH}_3 \rightarrow \text{c-}(\text{BH}_2\text{NH}<em>2)</em>{13} + 13\text{H}_2)</td>
<td>-217.7</td>
<td>-16.8</td>
</tr>
</tbody>
</table>

- Dative bond to B-N \(\sigma\) bond transition is always energetically favorable.
Energetics (kcal/mol) for H$_2$ release in polymeric chains

\[
\Delta H(\text{B3LYP}) = -4.4 \\
\Delta H(\text{G3MP2, 298 K}) = -4.1
\]

\[
\Delta H(\text{B3LYP}) = -42.9 \\
\Delta H(\text{G3MP2, 298 K}) = -40.8
\]

\[
\Delta H(\text{B3LYP}) = -32.8 \\
\Delta H(\text{G3MP2, 298 K}) = -34.6
\]

\[
\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3
\]

Donor-Acceptor N-B bond $\approx$ 1.66 Å
Normal N-B bond $\approx$ 1.56 Å

\[
\Delta H(\text{B3LYP}) = -42.9 \\
\Delta H(\text{G3MP2, 298 K}) = -40.8
\]

\[
\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2 + \text{H}_2
\]

Bridge structure
Donor-Acceptor N-B bond = 1.73 Å
Normal N-B bond $\approx$ 1.54 Å
B-H bond $\approx$ 1.34 Å

\[
\Delta H(\text{B3LYP}) = -32.8 \\
\Delta H(\text{G3MP2, 298 K}) = -34.6
\]

\[
\text{NH}_2\text{BHNHBHNHBH}_2 + 3\text{H}_2
\]
N-B bond = 1.42 Å and 1.45 Å

\[
\text{c-(NH}_2\text{BH}_2)_3
\]
N-B bond = 1.59 Å

• Evidence that polymer to polymer is not as exothermic as forming the ring – need condensed phase interactions.
Proposed cationic mechanism for chain growth:

\[ \text{H}_2\text{B}^+\text{NH}_3 + \text{H}_3\text{NBH}_3 \rightarrow \left[ \begin{array}{c} \text{H}_2\text{B}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right] \]

\[ \rightarrow \left[ \begin{array}{c} \text{H}_2\text{B}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ - \text{H}_2 \]

\[ \rightarrow \left[ \begin{array}{c} \text{H}_2\text{B}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ \]

\[ \text{H}_3\text{NBH}_3 \]

\[ \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ \]

\[ \left[ \begin{array}{c} \text{H}_2\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ \]

\[ \rightarrow \text{H}_3\text{NBH}_3 \]

\[ \rightarrow \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ - \text{H}_2 \]

\[ \rightarrow \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ \]

\[ \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ \]

\[ \rightarrow \text{H}_3\text{NBH}_3 \]

\[ \rightarrow \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ - \text{H}_2 \]

\[ \rightarrow \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ \]

\[ \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ \]

\[ \rightarrow \text{H}_3\text{NBH}_3 \]

\[ \rightarrow \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ - \text{H}_2 \]

\[ \rightarrow \left[ \begin{array}{c} \text{H}_3\text{B}^-\text{NH}_2^-\text{BH}^-\text{NH}_3 \\
\text{H} - \text{BH}_2^-\text{NH}_3 \end{array} \right]^+ \]
NMR Chemical Shifts: Cations

\[ \delta = 70.6 \]
\[ \text{BH}_2\text{NH}_2\text{CH}_3^+ \]

\[ \delta = -21.1 \]
\[ \delta = -19.0 \]
\[ \text{CH}_3\text{NHBH}_2\text{BH}_2\text{NH}_2\text{CH}_3 \]

\[ \delta = -19.1 \]
\[ \delta = -9.7 \]
\[ \delta = -22.0 \]
\[ \text{CH}_3\text{NHBH}_2\text{BH}_2\text{NHCH}_3\text{BH}_2\text{CH}_3^+ \]

- $^{11}$B chemical shifts can be reliably predicted at the DFT level and used to aid in the interpretation of experiment. Potential for bridging H and NH$_2^+$ groups exists in cationic polymer chains.
Proposed cationic mechanism for chain growth

Energy level diagram in kcal/mol

\[ \Delta H \text{ (kcal/mol)} \]

Generalized reaction coordinate

\[ \text{Generalized reaction coordinate} \]

\[ \begin{array}{c}
-98 \\
-46 \quad -45 \\
-55 \\
-69 \\
-71 \\
-75 \\
0
\end{array} \]

\[ H^+ + B(C_6F_5)_3 \text{H}^- \]

\[ H_2 + BH_3NH_3 \]

\[ H_2 + BH_3NH_3 \]

\[ + BH_3NH_3 \]

\[ + BH_3NH_3 \]
### Gas Phase Reaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{BH}_3 \rightarrow \text{BH}_2\text{NH}_3^+ + \text{BH}_4^-$</td>
<td>139</td>
</tr>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{B}($C$_6\text{H}_5$,)$_3 \rightarrow \text{BH}_2\text{NH}_3^+ + \text{B}($C$_6\text{H}_5$,)$_3$H$^-</td>
<td>139</td>
</tr>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{B}($C$_6\text{F}_5$,)$_3 \rightarrow \text{BH}_2\text{NH}_3^+ + \text{B}($C$_6\text{F}_5$,)$_3$H$^-</td>
<td>98</td>
</tr>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{BH}_2\text{NH}_3^+ + \text{HSO}_4^- + \text{H}_2</td>
<td>124</td>
</tr>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{BH}_2\text{NH}_3^+ + \text{CF}_3\text{SO}_3^- + \text{H}_2</td>
<td>115</td>
</tr>
</tbody>
</table>

### Salt reactions ($\pm$ 5 kcal/mol)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{BH}_3 \rightarrow \text{BH}_2\text{NH}_3^+ / \text{BH}_4^-</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{B}($C$_6\text{H}_5$,)$_3 \rightarrow \text{BH}_2\text{NH}_3^+ / \text{B}($C$_6\text{H}_5$,)$_3$H$^-</td>
<td>38.1</td>
</tr>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{B}($C$_6\text{F}_5$,)$_3 \rightarrow \text{BH}_2\text{NH}_3^+ / \text{B}($C$_6\text{F}_5$,)$_3$H$^-</td>
<td>1.6</td>
</tr>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{BH}_2\text{NH}_3^+ / \text{HSO}_4^- + \text{H}_2</td>
<td>-7.0</td>
</tr>
<tr>
<td>$\text{BH}_3\text{NH}_3 + \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{BH}_2\text{NH}_3^+ / \text{CF}_3\text{SO}_3^- + \text{H}_2</td>
<td>-9.6</td>
</tr>
</tbody>
</table>

### Lattice Energies

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$U_L$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BH}_2\text{NH}_3^+ / \text{B}($C$_6\text{F}_5$,)$_3$H$^-</td>
<td>96.9</td>
</tr>
<tr>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3^+(\text{bridge}) / \text{B}($C$_6\text{F}_5$,)$_3$H$^-</td>
<td>94.8</td>
</tr>
<tr>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3^+(\text{bridge}) / \text{B}($C$_6\text{F}_5$,)$_3$H$^-</td>
<td>92.6</td>
</tr>
</tbody>
</table>

- Need strong Lewis acids or very strong acids for this chemistry to work.
- Have the most extensive Lewis acidity scale available and strong Brönsted acid scale.
Regeneration of Ammonia Borane: Thermodynamics for Reprocessing Schemes – The 5 Step approach and what we can predict

Digestion: Mechanisms, bond energies

Activation: Mechanisms, bond energies

Reduction: Mechanisms, bond energies

Disproportionation: Mechanisms, reaction energies \(2\text{BHR}_2 \rightarrow \text{BH}_2\text{R} + \text{BR}_3\)

Ammoniation: Cone angles, steric effects, BH$_3$-L binding energies
<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2HB(OCH₃)₃⁻ → H₂B(OCH₃)₂⁻ + B(OCH₃)₄⁻</td>
<td>-1.4</td>
</tr>
<tr>
<td>HB(OCH₃)₃⁻ + H₂B(OCH₃)₂⁻ → H₃B(OCH₃)⁻ + B(OCH₃)₄⁻</td>
<td>-4.2</td>
</tr>
<tr>
<td>HB(OCH₃)₃⁻ + H₃B(OCH₃)⁻ → B(OCH₃)₄⁻ + BH₄⁻</td>
<td>-</td>
</tr>
<tr>
<td>11.4</td>
<td></td>
</tr>
<tr>
<td>2HAl(OCH₃)₃⁻ → H₂Al (OCH₃)₂⁻ + Al(OCH₃)₄⁻</td>
<td>0.3</td>
</tr>
<tr>
<td>HAl(OCH₃)₃⁻ + H₂Al (OCH₃)₂⁻ → H₃Al (OCH₃)⁻ + Al(OCH₃)₄⁻</td>
<td>-0.4</td>
</tr>
<tr>
<td>HAl(OCH₃)₃⁻ + H₃Al (OCH₃)⁻ → Al(OCH₃)₄⁻ + AlH₄⁻</td>
<td>-3.3</td>
</tr>
<tr>
<td>2HGa(OCH₃)₃⁻ → H₂Ga(OCH₃)₂⁻ + Ga(OCH₃)₄⁻</td>
<td>2.7</td>
</tr>
<tr>
<td>HGa(OCH₃)₃⁻ + H₂Ga (OCH₃)₂⁻ → H₃Ga (OCH₃)⁻ + Ga(OCH₃)₄⁻</td>
<td>2.6</td>
</tr>
<tr>
<td>HGa(OCH₃)₃⁻ + H₃Ga (OCH₃)⁻ → Ga(OCH₃)₄⁻ + GaH₄⁻</td>
<td>1.6</td>
</tr>
</tbody>
</table>

- Can predict H transfer reaction energies and see periodic trends
## Thermodynamics (kcal/mol) of Disproportionation/Conproportionation Equilibria: Hydride Transfer

### Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAl(OCH₃)₂⁺ + B(OCH₃)₄⁻ → Al(OCH₃)₃ + HB(OCH₃)₃⁻</td>
<td>16.5</td>
</tr>
<tr>
<td>HAl(CH₃)₂⁺ + B(OCH₃)₄⁻ → (CH₃)₂Al(OCH₃) + HB(OCH₃)₃⁻</td>
<td>12.8</td>
</tr>
<tr>
<td>HSi(CH₃)₃ + B(OCH₃)₄⁻ → (CH₃)₃Si(OCH₃) + HB(OCH₃)₃⁻</td>
<td>6.2</td>
</tr>
<tr>
<td>HSi(OCH₃)₃ + B(OCH₃)₄⁻ → Si(OCH₃)₄ + HB(OCH₃)₃⁻</td>
<td>2.1</td>
</tr>
<tr>
<td>HSn(CH₃)₃ + B(OCH₃)₄⁻ → (CH₃)₃Sn(OCH₃) + HB(OCH₃)₃⁻</td>
<td>21.7</td>
</tr>
<tr>
<td>HSn(OCH₃)₃ + B(OCH₃)₄⁻ → Sn(OCH₃)₄ + HB(OCH₃)₃⁻</td>
<td>25.5</td>
</tr>
<tr>
<td>HSi(CH₃)₃ + BCl₃ → ClSi(CH₃)₃ + HBCl₂</td>
<td>-7.8</td>
</tr>
<tr>
<td>HSi(CH₃)₃ + B(OCH₃)₃ → (OCH₃)Si(CH₃)₃ + HB(OCH₃)₂</td>
<td>8.2</td>
</tr>
<tr>
<td>HSi(CH₂CH₃)₃ + BCl₃ → ClSi(CH₂CH₃)₃ + HBCl₂</td>
<td>-8.3</td>
</tr>
<tr>
<td>HSi(CH₂CH₃)₃ + B(OCH₃)₃ → (OCH₃)Si(CH₂CH₃)₃ + HB(OCH₃)₂</td>
<td>9.4</td>
</tr>
<tr>
<td>HSi(OCH₃)₃ + BCl₃ → ClSi(OCH₃)₃ + HBCl₂</td>
<td>-5.9</td>
</tr>
<tr>
<td>HSi(OCH₃)₃ + B(OCH₃)₃ → Si(OCH₃)₄ + HB(OCH₃)₂</td>
<td>3.7</td>
</tr>
<tr>
<td>HSi(Ph)₃ + BCl₃ → ClSi(Ph)₃ + HBCl₂</td>
<td>-6.6</td>
</tr>
<tr>
<td>HSi(Ph)₃ + B(OCH₃)₃ → (OCH₃)Si(Ph)₃ + HB(OCH₃)₂</td>
<td>7.5</td>
</tr>
</tbody>
</table>

- Can transfer H from trialkyl silanes to BCl₃ but not to B(OCH₃)₃. Consistent with experimental observations.
Planned Experimental Activities

• Continue synthesis and characterization of cyanocarbons for H₂ storage – Develop molecules with improved weight percent and as structural components.
  - Extend newly discovered pyridazine chemistry to improve performance and weight percent hydrogen
• Continue synthesis and characterization of carbenes to improve performance and weight percent hydrogen.
  - Continue studies on imidazol(in)ium borohydrides and carbene-borane adducts
• Develop improved synthesis of and continue characterization of newly discovered phosphocarbons for improved hydrogen release characteristics.
New Experimental Opportunities: More Main Group Chemistry and a way to improve the weight percent

A new, non-metallic, uncatalyzed hydrogen storage system: \( \text{H}_2 \) release at ambient temperature & pressure.

Water reduction - extends range of hydrogen storage in 1,1- and 1,2-elimination systems.
Planned Computational Activities

• Predict Thermodynamics for reactions:
  - Borane-amine chemistry to optimize and control the H₂ release process
  - Reprocessing: B-O to B-H regeneration. Predict the energetics and kinetics of key steps in 5-step process to optimize experimental approach.
  - Continue to predict the energetics for larger boron hydrides and salts following our efforts on \((\text{B}_{12}\text{H}_{12})^{2-}(\text{NH}_4^+)_{2}\)
  - Complete studies on borane-amine ionic pathway energetics
  - Develop approaches to predict intermolecular interactions and heats of vaporization/fusion and complete studies of borane amine thermodynamics
  - Continue to incorporate solvent effects
  - Continue prediction of thermodynamics and kinetics for carbenes and cyanocarbons including pyridazines
  - Predict thermodynamic and kinetics of phosphocarbons

• Develop improved reaction mechanisms based on predictions of reaction kinetics to optimize processes

• Use computational approaches to design new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metals

• Predict spectroscopic properties (nmr, IR/Raman, UV-vis) for use in analyzing experimental data

• Manage Center website and develop data archival capability
Summary

• Developed new conceptual models for improving weight percent beyond 1:1 stoichiometry to enable us to meet DOE 2015 goals. Developed thermodynamic approach to meet desorption temperature and plateau pressures.

• Developed carbene and carbenium ion chemistry to meet DOE 2010 goals.

• Developed new cyanocarbon chemistry to meet DOE 2010 goals.
  - Discovered new pyradizine compound to manage conformational issues

• 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.
  - Carbenes and cyanocarbons
  - Borane-amines and isoelectronic molecules
  - Borane-amine reaction mechanism
  - Borane-amine regeneration mechanisms
# UA - 2006
On-Board Hydrogen Storage System Targets

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>DOE 2010 System Targets</th>
<th>carbene</th>
<th>cyanocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight % $H_2$</td>
<td>6%</td>
<td>2%</td>
<td>1%</td>
</tr>
<tr>
<td>Dehydrogenation Rate</td>
<td>0.02g/s-kW</td>
<td>In progress</td>
<td>Oxidation step diffusion limited</td>
</tr>
<tr>
<td>Storage Efficiency Center Goal</td>
<td>Near thermoneutral 70%</td>
<td>Exothermic: -5 kcal/mol Ultimate: Thermoneutral</td>
<td>Endothermic: 5 kcal/mol Ultimate: Thermoneutral</td>
</tr>
</tbody>
</table>

*Data is based on material only, not system value*
Publications and Presentations


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


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.