Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

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The University of Alabama
DOE Center of Excellence for Chemical Hydrogen Storage
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Project ID # ST30

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## Overview

### Timeline
- Project start date: Jan. 05
- Project end date: FY10
- Percent complete: 50%

### Barriers
- DOE Barriers addressed
  - System Cost
  - System Weight and Volume
  - Spent Fuel Regeneration

### Budget
- Projected total project funding: $2,288,053
  - DOE share: $1,540,567 (requested)
  - UA share: $747,486
- Funding for FY05: $431K
  - $225K (DOE), $206K (UA)
- Funding for FY06: $480K
  - $350K (DOE), $130K (UA)
- Funding for FY07: $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, Millenium Cell, Rohm and Haas, and US Borax.
Objectives

• Develop promising approaches to chemical H₂ storage for future DOE targets.

• 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 by improving the energy balance. This will provide longer term alternatives.

• Develop and implement imidazolium (carbene) based H₂ activation chemistry.

• Develop and implement systems based on main group elements. Examples: nitrogen and phosphorus.

• 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 and develop new materials that meet the DOE targets.
Approach

• Develop and identify new concepts to increase capacity and minimize weight (Example: Use storage medium for structural benefits.)
• Develop new concepts to improve energy balance. Especially relevant for ease of H₂ release/regeneration of H₂ storage system.
• Develop new approaches to release hydrogen from dihydroimidazoles, based on new chemistry and our world leadership in stable carbene chemistry.
• Demonstrate proof of concepts and key reactions.
• Key issue is to minimize weight by eliminating substituents or changing them into components that can store H₂ while maintaining kinetic and thermodynamic properties.
• Use highly accurate 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 (regeneration).
• 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.

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), Jackson R. Switzer (undergrad), Jacob R. Batson (undergrad), Minh T. Nguyen (visiting faculty)
Accomplishments

UA Experimental Studies
• Developed first tetracyanoethylene (TCNE) oligomerization procedure for making cyanocarbons for H₂ storage with potential of 11 weight %.
• Continued work on 4-member ring diradicals with P substituents shows H₂ addition and release. Serves as first model for H₂ release from C at room temperature.
• Initial studies demonstrate catalyst photoactivation for H₂ addition to cyanocarbons & carbenes. Potential for widespread applicability.
• Demonstrated weight reduction by oligomerization of carbenes. Demonstrated oxidized and reduced (H₂ on and off) carbenes. Develop mixed carbene/TCNE synthesis to make oligomers.

UA Computational Studies
• 1st set of accurate thermodynamics for BₓNₓHᵧ compounds up to x = 3 and y = 14 for release and regeneration of AB (with PNNL).
• Accurate bond energies for AB (ammonia borane = BH₃NH₃) & derived systems for release and regeneration. (Center)
• H₂ release processes from AB (BH₃ as a Lewis acid catalyst). (LANL + Center)
• H₂ release processes studied via cationic chain polymerization mechanism (with LANL).
• First reliable thermodynamic properties of B₃H₇NH₃ and decomposition mechanism. (Penn)
• Study mechanism of H₂ release from AB dimer (BH₃NH₃)₂ and from zwitterionic isomer [NH₃BH₂NH₃⁺][BH₄⁻] – importance of seeding. (PNNL)
• Methyl substituent effects on energetics of borane amine compounds for release and regeneration (mixed solvents). (LANL, PNNL, UW, Penn, NAU)
• Extensive studies of energetics for H₂ AB regeneration mechanisms. (LANL, PNNL, Penn, UC-Davis, U. Washington).
• Energetics for novel chemical H₂ storage systems: carbenes, cyanocarbons, P-based diradicals.
Thermodynamic Properties of BN Compounds in Different Phases at 298 K (CCSD(T) + Expt)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>$\Delta H_f^\circ$ 298 K kcal/mol</th>
<th>$S^\circ$ 298 K cal/mol·K</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_3$NH$_3$</td>
<td>gas</td>
<td>-13.5 ± 1.0</td>
<td>57.1</td>
<td>Calc</td>
</tr>
<tr>
<td></td>
<td>solid</td>
<td>-36.6 ± 2.4</td>
<td>23.0</td>
<td>Expt</td>
</tr>
<tr>
<td>B$_3$N$<em>3$H$</em>{12}$</td>
<td>gas</td>
<td>-96.6 ± 1.0</td>
<td>79.3</td>
<td>Calc</td>
</tr>
<tr>
<td></td>
<td>solid</td>
<td>-120.5 ± 4</td>
<td>21.0</td>
<td>Expt</td>
</tr>
<tr>
<td>B$_3$N$_3$H$_6$</td>
<td>gas</td>
<td>-121.9 ± 3</td>
<td></td>
<td>Expt</td>
</tr>
<tr>
<td></td>
<td>liquid</td>
<td>-129.0 ± 3</td>
<td>47.7</td>
<td>Expt</td>
</tr>
<tr>
<td></td>
<td>gas</td>
<td>-115.5 ± 1.0</td>
<td>68.7</td>
<td>Calc</td>
</tr>
<tr>
<td></td>
<td>liquid</td>
<td>-122.6 ± 1.1</td>
<td></td>
<td>Calc + Expt</td>
</tr>
<tr>
<td></td>
<td>solid</td>
<td>-123.6 ± 1.6</td>
<td></td>
<td>Calc + Expt</td>
</tr>
</tbody>
</table>

$\Delta H_f^\circ$ from calc $\Delta H_f^\circ$ gas + expt $\Delta H_{sub}$ $S^\circ$ from expt

First complete set of high level values for use in regeneration and release studies for AB.
### Accurate Heats of Formation for B-N Compounds

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta H_f(0 \text{ K})$</th>
<th>$\Delta H_f(298 \text{ K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_3$NH$_3$</td>
<td>-9.1</td>
<td>-13.5</td>
</tr>
<tr>
<td>2a</td>
<td>-85.3</td>
<td>-96.6</td>
</tr>
<tr>
<td>2b</td>
<td>-84.3</td>
<td>-95.5</td>
</tr>
<tr>
<td>3</td>
<td>-109.3</td>
<td>-115.5</td>
</tr>
<tr>
<td>4</td>
<td>-46.4</td>
<td>-53.6</td>
</tr>
<tr>
<td>5</td>
<td>-79.8</td>
<td>-87.5</td>
</tr>
<tr>
<td>6</td>
<td>-64.1</td>
<td>-71.8</td>
</tr>
<tr>
<td>7</td>
<td>-75.9</td>
<td>-85.3</td>
</tr>
<tr>
<td>8a</td>
<td>-27.4</td>
<td>-35.3</td>
</tr>
<tr>
<td>8b</td>
<td>-39.2</td>
<td>-47.6</td>
</tr>
<tr>
<td>9a</td>
<td>-48.5</td>
<td>-59.9</td>
</tr>
<tr>
<td>9b</td>
<td>-72.1</td>
<td>-84.3</td>
</tr>
<tr>
<td>10</td>
<td>-37.2</td>
<td>-43.9</td>
</tr>
<tr>
<td>11</td>
<td>-52.6</td>
<td>-62.8</td>
</tr>
<tr>
<td>12</td>
<td>-32.2</td>
<td>-41.3</td>
</tr>
<tr>
<td>13</td>
<td>25.4</td>
<td>20.4</td>
</tr>
<tr>
<td>14</td>
<td>-84.6</td>
<td>-91.2</td>
</tr>
<tr>
<td>BH$_2$NH$_2$</td>
<td>-15.9</td>
<td>-18.6</td>
</tr>
</tbody>
</table>
Accurate Bond Energies for B-N Compounds (in kcal/mol at 298 K)

BN Dissociation for Cyclotriborazane

\[
\text{BH}_3\text{NH}_3 \rightarrow \text{BH}_3 + \text{NH}_3 \quad \Delta H = 33.8 \text{ kcal/mol}
\]

BN Dissociation for Cyclodiborazane

\[
\text{BH}_2\text{NH}_2 \rightarrow \text{BH}_2 + \text{NH}_2 \quad \Delta H = 27.7 \text{ kcal/mol}
\]

BN Dissociation for Borazine

\[
\text{BH}_3\text{NH}_3 \rightarrow \text{BH}_3 + \text{NH}_3 \quad \Delta H = 135.9 \text{ kcal/mol}
\]

\[
\text{BH}_2\text{NH}_2 \rightarrow \text{BH}_2 + \text{NH}_2 \quad \Delta H = 141.8 \text{ kcal/mol}
\]

Bond energies provide insights into mechanism design. Example: First release of \( \text{H}_2 \) from \( \text{AB} \) is driven by transition from dative B-N sigma bond to strong B-N sigma bond. Shows inherent instabilities of intermediates. Provides insights into ring formation vs. chain formation.
Reaction Pathway for $H_2$ Generation from $BH_3NH_3$

B-N bond cleavage is energetically more favored over the unimolecular $H_2$ release from borane amine.

$BH_3NH_3 \rightarrow BH_2NH_2 + H_2$

$BH_3NH_3 + BH_3 \rightarrow BH_2NH_2 + H_2 + BH_3$

$BH_3$ can serve as a Lewis acid catalyst for $H_2$ elimination from $BH_3NH_3$. 
One or two $\text{H}_2$ molecules can be released through direct pathways with barrier heights ranging from 47 to 52 kcal/mol, relative to the dimer and 33 to 38 kcal/mol relative to 2 monomers. Energies are too high for this process to play a role.

$[\text{BH}_4^-][\text{NH}_3\text{BH}_2\text{NH}_3]^+$ is $\sim 13$ kcal/mol less stable than $(\text{AB})_2$. $\text{H}_2$-release is characterized by a much lower energy barrier of $\sim 20$ kcal/mol. Consistent with seeding of AB with the zwitterion leading to improved rates. No low-energy unimolecular rearrangements connecting AB dimer with zwitterion.
### Thermodynamics (kcal/mol) of Disproportionation/Conproportionation Equilibria at 298 K

<table>
<thead>
<tr>
<th>Digestion Reaction</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_3\text{N}_3\text{H}_6 + 6\text{HF} \rightarrow 3\text{NH}_3 + 3\text{HBF}_2$</td>
<td>-53.7</td>
</tr>
<tr>
<td>$\text{B}_3\text{N}_3\text{H}_6 + 6\text{HCl} \rightarrow 3\text{NH}_3 + 3\text{HBCl}_2$</td>
<td>38.7</td>
</tr>
<tr>
<td>$\text{B}_3\text{N}_3\text{H}_6 + 6\text{HBr} \rightarrow 3\text{NH}<em>3 + 3\text{HBB}</em>{\text{Br}_2}$</td>
<td>60.5</td>
</tr>
<tr>
<td>$\text{B}_3\text{N}_3\text{H}_6 + 6\text{H}_2\text{O} \rightarrow 3\text{NH}_3 + 3\text{HB(OH)}_2$</td>
<td>-30.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disproportionation Reaction</th>
<th>G3MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{HB(OH)}_2 \rightarrow \text{H}_2\text{B(OH)} + \text{B(OH)}_3$</td>
<td>3.8</td>
</tr>
<tr>
<td>$\text{H}_2\text{B(OH)} + \text{HB(OH)}_2 \rightarrow \text{BH}_3 + \text{B(OH)}_3$</td>
<td>4.8</td>
</tr>
<tr>
<td>$2\text{H}_2\text{B(OH)} \rightarrow \text{BH}_3 + \text{HB(OH)}_2$</td>
<td>1.0</td>
</tr>
<tr>
<td>$2\text{HB(OCH}_3)_2 \rightarrow \text{H}_2\text{B(OCH}_3) + \text{B(OCH}_3)_3$</td>
<td>3.2</td>
</tr>
<tr>
<td>$\text{H}_2\text{B(OCH}_3) + \text{HB(OCH}_3)_2 \rightarrow \text{BH}_3 + \text{B(OCH}_3)_3$</td>
<td>6.9</td>
</tr>
<tr>
<td>$2\text{H}_2\text{B(OCH}_3) \rightarrow \text{BH}_3 + \text{HB(OCH}_3)_2$</td>
<td>3.7</td>
</tr>
<tr>
<td>$2\text{HB(NH}_2)_2 \rightarrow \text{H}_2\text{B(NH}_2) + \text{B(NH}_2)_3$</td>
<td>6.0</td>
</tr>
<tr>
<td>$\text{H}_2\text{B(NH}_2) + \text{HB(NH}_2)_2 \rightarrow \text{BH}_3 + \text{B(NH}_2)_3$</td>
<td>19.2</td>
</tr>
<tr>
<td>$2\text{H}_2\text{B(NH}_2) \rightarrow \text{BH}_3 + \text{HB(NH}_2)_2$</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Use as input for the experimental design of reaction steps. Reactions involving OR lead to exothermic or thermoneutral reactions. Need to form NH$_4$X for halogens.
Disproportionation Chemistry (kcal/mol)

B3LYP/DGDZVP2

\[ \Delta H (0K) \]

2BH\(_2\)X \rightarrow BH\(_2\)X + BX\(_3\)  
2HB(OH)\(_2\) \rightarrow H\(_2\)B(OH) + B(OH)\(_3\)  
2HB(OCH\(_3\))\(_2\) \rightarrow H\(_2\)B(OCH\(_3\)) + B(OCH\(_3\))\(_3\)  
2HB(OPh)\(_2\) \rightarrow H\(_2\)B(OPh) + B(OPh)\(_3\)  
2HB(OPhF\(_5\))\(_2\) \rightarrow H\(_2\)B(OPhF\(_5\)) + B(OPhF\(_5\))\(_3\)  

BH\(_2\)X + BHX\(_2\) \rightarrow BH\(_3\) + BX\(_3\)

H\(_2\)B(OH) + HB(OH)\(_2\) \rightarrow BH\(_3\) + B(OH)\(_3\)  
H\(_2\)B(OCH\(_3\)) + HB(OCH\(_3\))\(_2\) \rightarrow BH\(_3\) + B(OCH\(_3\))\(_3\)  
H\(_2\)B(OPh) + HB(OPh)\(_2\) \rightarrow BH\(_3\) + B(OPh)\(_3\)  
H\(_2\)B(OPhF\(_5\)) + HB(OPhF\(_5\))\(_2\) \rightarrow BH\(_3\) + B(OPhF\(_5\))\(_3\)  

2H\(_2\)BX \rightarrow BH\(_3\) + HBX\(_2\)

2H\(_2\)B(OH) \rightarrow BH\(_3\) + HB(OH)\(_2\)  
2H\(_2\)B(OCH\(_3\)) \rightarrow BH\(_3\) + HB(OCH\(_3\))\(_2\)  
2H\(_2\)B(OPh) \rightarrow BH\(_3\) + HB(OPh)\(_2\)  
2H\(_2\)B(OPhF\(_5\)) \rightarrow BH\(_3\) + HB(OPhF\(_5\))\(_2\)  

Optimize substituents on O for digestion reactions.
Optimize Regeneration Schemes 298 K (kcal/mol)

\[ \Delta H \]

1. \( \frac{1}{3}(\text{B}_3\text{N}_3\text{H}_6) \text{ (s)} + 4\text{HBr (g)} \rightarrow \text{NH}_4\text{Br (s)} + \text{BBr}_3 \text{ (l)} + \text{H}_2 \text{ (g)} \)
   \(-45.8\)

2. \( \text{BBr}_3 \text{ (l)} + 3\text{HSn(Bu)}_3 \text{ (l)} + \text{NH}_3 \text{ (g)} \rightarrow \text{BH}_3\text{NH}_3 \text{ (s)} + 3\text{BrSn(Bu)}_3 \text{ (l)} \)
   \(-82.8\)

3. \( \text{NH}_4\text{Br (s)} \rightarrow \text{HBr (g)} + \text{NH}_3 \text{ (g)} \)
   \(45.1\)

4. \( 3\text{BrSn(nBu)}_3 \text{ (l)} + 3\text{H}_2 \text{ (g)} \rightarrow 3\text{HBr (g)} + 3\text{HSn(nBu)}_3 \text{ (l)} \)
   \(88.2\)

**Overall reaction:** \( \frac{1}{3}(\text{B}_3\text{N}_3\text{H}_6) \text{ (s)} + 2\text{H}_2 \rightarrow \text{BH}_3\text{NH}_3\text{(s)} \)
\(\Delta H = 4.7\)

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

\[
\frac{(2 \times 58)}{(3 \times 58 + 133 - (x\%) \times 129) = 0.38 \text{ for } 0\% \text{ heat recovery}}
\]

More H\(_2\) release

Less use lower endo

Improve heat recovery

Raise efficiency

\[ \Delta H \]

1. \( \frac{1}{2}(\text{B}_3\text{N}_3\text{H}_6) \text{ (s)} + 4\text{HCl (g)} \rightarrow \text{NH}_4\text{Cl (s)} + \text{BCl}_3 \text{ (l)} + \text{H}_2 \text{ (g)} \)
   \(-47.8\)

2. \( \text{BCl}_3 \text{ (l)} + 3\text{HSi(Et)}_3 \text{ (l)} + \text{NH}_3 \text{ (g)} \rightarrow \text{BH}_3\text{NH}_3 \text{ (s)} + 3\text{ClSi(Et)}_3 \text{ (l)} \)
   \(-77^*\)

3. \( \text{NH}_4\text{Cl (s)} \rightarrow \text{HCl (g)} + \text{NH}_3 \text{ (g)} \)
   \(42.1\)

4. \( 3\text{ClSi(Et)}_3 \text{ (l)} + 3\text{H}_2 \text{ (g)} \rightarrow 3\text{HCl (g)} + 3\text{HSi(Et)}_3 \text{ (l)} \)
   \(88^*\)

Optimize reaction energies and provide limitations to processes
### B-H & Si-H Bond Energies (kcal/mol)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta H_f$</th>
<th>$D_e$(B-H) $^{CCSD(T)/CBS}$</th>
<th>$D_e$(Si-H) $^{CCSD(T)/CBS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_2$SiH$_3$</td>
<td>41.4</td>
<td>101.1</td>
<td>76.4</td>
</tr>
<tr>
<td>HBSiH$_3$</td>
<td>90.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$BSiH$_2$</td>
<td>66.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_3$BSiH$_3^-$</td>
<td>-14.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH(SiH$_3$)$_2$</td>
<td>55.4</td>
<td>96.4(95.5)</td>
<td>76.0(74.6)</td>
</tr>
<tr>
<td>B(SiH$_3$)$_2$</td>
<td>100.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HB(SiH$_3$)(SiH$_2$)</td>
<td>79.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(SiH$_3$)$_3$</td>
<td>68.7</td>
<td>74.9(73.2)</td>
<td></td>
</tr>
<tr>
<td>B(SiH$_3$)$_2$(SiH$_2$)</td>
<td>91.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$Si(BH$_2$)$_2$</td>
<td>72.2</td>
<td>76.2(69.8)</td>
<td>71.9(71.9)</td>
</tr>
<tr>
<td>HSi(BH$_2$)$_2$</td>
<td>92.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$Si(BH$_2$)(BH)</td>
<td>96.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSi(BH$_2$)$_3$</td>
<td>100.4</td>
<td>101.0(100.2)</td>
<td>70.8(72.9)</td>
</tr>
<tr>
<td>Si(BH$_2$)$_3$</td>
<td>119.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSi(BH$_2$)$_2$(BH)</td>
<td>149.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(BH$_2$)$_4$</td>
<td>131.1</td>
<td>99.9(99.3)</td>
<td></td>
</tr>
<tr>
<td>Si(BH$_2$)$_3$(BH)</td>
<td>179.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- B-H bond energies are larger than Si-H bond energies for most molecules. B-H bond energies have more dependence on structure. Regeneration with Si nanoparticles.
- Si-H bond energies are not strongly dependent on substituent.
- Calculate activation energy to remove H$_2$ from Si$_x$H$_y$ clusters and doped clusters. What is the role of strain?

The heats of formation for the molecules BH$_2$SiH$_3$, HBSiH$_3$, H$_2$BSiH$_2$, and H$_3$BSiH$_3^-$ $^{CCSD(T)/CBS}$ level. Energies in () are at the G3MP2 level.
Heteroatom Organic Systems for Hydrogen Storage: The “Alabama Approach”

1,1 - elimination to give carbene products

- Hydrogen elimination is symmetric (non-polar (*) )
- Metal catalyst required (currently substituents on N, C)
- Endothermic dehydrogenation, $P_{eq} < 1 \text{ atm}$

Ultimate: 7.2 %
Currently: 2 % (1.8 % with catalyst)

Water reduction - extend range of hydrogen storage in 1,1- and 1,2-elimination systems

Ultimate: 8.0 %
Currently: 0.6 %

1,5 - elimination to give fused diimidazolium rings

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

Ultimate: 7.2 %
Currently: 2.5 %
**UA Summary Table**

<table>
<thead>
<tr>
<th>Storage Parameter: DOE 2010 System Targets</th>
<th>Carbene</th>
<th>Cyanocarbon</th>
<th>Phosphacarbons*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Gravimetric Capacity: 6 wt%</td>
<td>Current: 2%</td>
<td>Current: &lt;1%</td>
<td>Current: &lt;1%</td>
</tr>
<tr>
<td></td>
<td>Ultimate: 7.2%</td>
<td>Ultimate**: 7.2%</td>
<td>Ultimate: 5% with P 7.2% by substituting N for P</td>
</tr>
<tr>
<td>Material Volumetric Capacity: 0.045 kg/L</td>
<td>Current: 0.045</td>
<td>Current: 0.045</td>
<td>Ultimate(P): 0.10</td>
</tr>
<tr>
<td></td>
<td>Ultimate: 0.098</td>
<td>Ultimate: 0.092</td>
<td>Ultimate(N): 0.092</td>
</tr>
<tr>
<td>Dehydrogenation Rate 0.02g/s-kW</td>
<td>In progress</td>
<td>Oxidation step diffusion limited</td>
<td>Model study</td>
</tr>
<tr>
<td>Storage Efficiency Center Goal: 50%</td>
<td>Exothermic: -5 kcal/mol</td>
<td>Endothermic: 5 kcal/mol</td>
<td>Model study</td>
</tr>
<tr>
<td></td>
<td>Ultimate: Thermoneutral</td>
<td>Ultimate: Thermoneutral</td>
<td></td>
</tr>
</tbody>
</table>

* Continue only as a model system to understand release and regeneration

** Ultimate for CN polymer is C₂N₂H₆ = 10.3%
Alternative Approach to Increase H\textsubscript{2} Weight Percent: Incorporate H\textsubscript{2}O into the Reduction Cycle

\[ A + H\textsubscript{2}O \rightarrow B \text{ (DFT/B3LYP)} \]

- MH = “metal” or organic hydride
- MO = “metal” oxide
- Works with NaH/LiH/KH at 25°C

$B$ trans linear \[ \Delta H(298K) = -33.1 \quad \Delta G(298K) = -24.4 \]

$B$ cis linear \[ \Delta H(298K) = -32.4 \quad \Delta G(298K) = -23.8 \]

$B$ trans twisted \[ \Delta H(298K) = -32.2 \quad \Delta G(298K) = -22.8 \]

$B$ cis twisted \[ \Delta H(298K) = -33.1 \quad \Delta G(298K) = -24.2 \]

Need to eliminate adamantyl substitutents due to weight issues. Potentially go to polyethylene diamine.

T = 25 °C

80 to 85% yield
1,1-Elimination for Hydrogen Storage: Increasing Capacity

How to increase capacity by making more effective use of substituents? 2 to 3 ring storage units and oligomerization

• Fuse 3 dihydroimidazole rings into “propellane” structure.
• Lightest possible material is $C_5H_{12}N_6$, forming $C_5H_6N_6 + 3 \text{H}_2$ (3.9 wt %)
• Reaction currently under study for N-substituted analogs

• Ultimate material with lateral condensation with $-\text{CH}_2-$ links gives $C_8H_{12}N_6$, forming $C_8N_6 + 6 \text{H}_2$ (6.3 wt %)
• Routes to such materials under study. Precursor is urea-based compound
• Poly-carbene product
First Synthesis of Tris(carbene) Precursor

1. 1 is generated from uric acid in a single step in high yield.
2. Interconversion of Tricyclics and First Synthesis of Fused Diimidazolium Rings for 1,5 Hydrogen Elimination Reactions
3. Dehydrogenate to make tricarbene.
Alternative Route 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

- Demonstrated oxidation to produce HI
- Need to demonstrate complete hydrogenation cycle
- Find appropriate catalyst
Poly-functional Cores for H₂ Storage: Future Focus

Steps 1 to 3 demonstrated
Step 4 done on tricyclic
Step 5 to be demonstrated

Bis-carbene as a model for an extended polymer

7.2 weight %, oligomer of TCNE (C₆N₄)
Cyanocarbons for Hydrogen Storage

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

Can we use derivatives of cyanocarbons for chemical H₂ storage systems?
Need to understand chemistry of the azo linkage that appear in cyanocarbon oligomers

Materials prepared having both hydrazine and triazine moieties

Ultimate: 7.5%
Currently: 0.5%

- Polymers based on these moieties, idealized composition: C₃H₉N₆ → C₃N₆ + 4.5 H₂ (7.0 wt % H₂)
- Combines both hexahydrotriazine → triazine, and hydrazo → diaza dehydrogenation concepts, expected to be more robust than unsubstituted hexahydrotriazine
- Expect will have similar needs for effective hydrogenation/dehydrogenation catalysts as hexahydrotriazine
- Substitution of an organic group for the H can dramatically change the energetics making favorable materials for H₂ release

(CH₃)HNNH(CH₃) → (CH₃)N=N(CH₃) + H₂  \( \Delta H \) (298 K) = -13.8, \( \Delta G \) (298 K) = -5.1 kcal/mol
Reactions of Carbenes with TCNE

Central polycyanocarbon core designed for easy reduction (H₂ addition)

At longer reaction times dimer dissociates to generate pendant polycyanocarbon carbene • 1.5 TCNE

H₂ + H⁺ reduced pendant group

C₂₀H₂₀N₈ → C₂₀H₂₂N₈H₂

Pd/C

• Control chemistry & improve H₂ storage capacity
• New catalysts

FAB-MS
UA: Future Experimental Work

- Synthesize extended carbene polymers (11.1 weight %, oligomer of TCNE (C₆N₄))

- Synthesis: Lower substituent weight % for carbenes

- Non-metal catalyst for H₂ release for carbenes & TCNE
  - Start with cyanocarbon radical anion (replaces Cl⁻ and takes H⁺)
  - Leuco-Methylene blue (colorless) delivers H⁻ to neutral cyanocarbon to form dihydrogenated anion and catalytic cycle restarts.

- Synthesize extended oligocarbene polymers from carbene chemistry

- Continue catalyst design for H₂ release for carbenes
Future Computational Work: Examples

• Continue to support overall center efforts in H\textsubscript{2} release, AB regeneration, new concepts including alternative inorganic and organic compounds and mechanisms.
  - Use density functional theory (DFT) benchmarked by accurate methods.
  - Calculate thermodynamics and kinetics.
  - Predict reaction mechanisms.
• Hydrogenation of TCNE. Which sites in what order? Hydrogenation of polycarbene- how?
• Release of H\textsubscript{2} from silanes for modeling nanocluster chemistry for regeneration.
• Computational design of new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metals. Release and regeneration.
• B-H regeneration. Predict energetics and kinetics of key steps (examples: digestion, reduction, etc.) to optimize experimental approach.
• Predict spectroscopic properties (nmr, IR/Raman, UV-vis) for use in analyzing experimental data.
• Develop improved reaction mechanisms based on predictions of reaction kinetics to optimize processes.
• Ammonia borane/ammonia triborane reactions – AB polymers from anionic polymerization.