High Level Computational Chemistry Approaches to the Prediction of the Energetic Properties of Chemical Hydrogen Storage Systems

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Chemical H₂ Storage Center of Excellence

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Robert Ramsay Chair Fund
The Promise of Chemical Hydrogen Storage

- Chemical reaction releases $H_2$ at suitable pressures and temperatures
  - Reaction *thermodynamics* dictate max. $H_2$ pressure as function of $T$ – need to manage both $\Delta H$ and $\Delta G$
  - Reaction *kinetics* dictate rate of release of $H_2$ – need to develop catalysts to control kinetics and release
  - Enables significant storage capacity at “zero” pressure – improve safety issues
- Infrastructure based on a solid or liquid fuel
  - Spent fuel regenerated “off-board” using industrial chemical engineering process technology to reduce cost
  - Bypass direct consumer contact with gaseous hydrogen
  - Hydrogen need only appear when required at the fuel cell anode
What’s needed for chemical accuracy?

Example: reaction energetics, catalyst design, or separations systems for hydrogen storage

Catalyst design will require quantitative information about transition states for critical reaction processes in catalysis. These are only accessible by computational methods, which hold the key to the fundamental understanding of catalytic processes thus enabling reliable catalyst design.

Predict equilibrium chemistry: Selectivity

<table>
<thead>
<tr>
<th>$K_{eq}$</th>
<th>Selectivity</th>
<th>$\Delta G$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50:50</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>90:10</td>
<td>1.4</td>
</tr>
<tr>
<td>100</td>
<td>99:1</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Predict accurate rates: Reactivity

Absolute Rates @ 298 K

Factor of 10 in rate @ 25°C is a change in $E_a$ of 1.4 kcal/mol

Molecular design will require being able to do accurate calculations and/or being very clever!
Solving the Schrödinger Equation

Molecular Orbital Theory
- Correlation Energy – CCSD(T), MPn, CASPT₂, MRCI
- Basis set – aug-ccpVnZ
- Environment
- Relativity

Density Functional Theory
- Exchange-Correlation Functional
  - Local
  - Gradient corrected
    - Becke-Perdew
    - B3LYP
    - Handy, etc
  - New approaches: OEP for exchange, new correlation
- Basis set
- Environment
- Relativity

Full CI
Total atomization energy at the CCSD(T) level extrapolated to the complete basis set limit using the augmented-correlation consistent basis sets

- + core-valence corrections
- + scalar relativistic
- + spin orbit
- + zero point energy
- + thermal corrections (0 → 298K)

Use atomic heats of formation to get molecular heats of formation

Use CCSD(T) or MP2 geometries

IP’s and EA’s
Carbenes for H₂ Storage Systems

Do 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
### Calculated atomization energies for carbenes

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CCSD(T)/CBS</th>
<th>$\Delta E_{ZPE}$</th>
<th>$\Delta E_{CV}$</th>
<th>$\Delta E_{SR}$</th>
<th>$\Delta E_{SO}$</th>
<th>$\sum D_0 \ (0K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbene</td>
<td>922.38</td>
<td>43.78</td>
<td>3.93</td>
<td>-1.15</td>
<td>-0.24</td>
<td>881.14</td>
</tr>
<tr>
<td>$^3$carbene</td>
<td>834.15</td>
<td>45.10</td>
<td>3.78</td>
<td>-1.23</td>
<td>-0.24</td>
<td>791.36</td>
</tr>
<tr>
<td>carbH$_2$</td>
<td>1052.90</td>
<td>57.85</td>
<td>3.99</td>
<td>-1.15</td>
<td>-0.24</td>
<td>997.65</td>
</tr>
<tr>
<td>carbH$^+$</td>
<td>865.93</td>
<td>52.11</td>
<td>4.27</td>
<td>-1.21</td>
<td>-0.24</td>
<td>816.64</td>
</tr>
<tr>
<td>carbH$^-$</td>
<td>952.83</td>
<td>47.58</td>
<td>3.55</td>
<td>-1.18</td>
<td>-0.24</td>
<td>1125.84</td>
</tr>
<tr>
<td>carbH</td>
<td>962.78</td>
<td>53.23</td>
<td>4.11</td>
<td>-1.24</td>
<td>-0.24</td>
<td>912.18</td>
</tr>
<tr>
<td>CarbH$_6$</td>
<td>1047.49</td>
<td>57.93</td>
<td>3.85</td>
<td>-1.20</td>
<td>-0.24</td>
<td>907.38</td>
</tr>
<tr>
<td>carbH$_8$</td>
<td>1196.52</td>
<td>73.07</td>
<td>3.87</td>
<td>-1.24</td>
<td>-0.24</td>
<td>1,125.84</td>
</tr>
</tbody>
</table>
## Carbene CCSD(T) Heats of Formation (kcal/mol)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CCSD(T) (0K)</th>
<th>CCSD(T) (298K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbene</td>
<td>60.4</td>
<td>55.4</td>
</tr>
<tr>
<td>$^3$carbene</td>
<td>150.2</td>
<td>145.9</td>
</tr>
<tr>
<td>carbene$H_2$</td>
<td>47.1</td>
<td>41.5</td>
</tr>
<tr>
<td>carbene$H^+$</td>
<td>176.5</td>
<td>171.6</td>
</tr>
<tr>
<td>carbene$H^-$</td>
<td>85.8</td>
<td>80.7</td>
</tr>
<tr>
<td>carbeneH</td>
<td>81.0</td>
<td>75.7</td>
</tr>
<tr>
<td>Carbene$H_6$</td>
<td>52.8</td>
<td>46.8</td>
</tr>
<tr>
<td>Carbene$H_8$</td>
<td>22.2</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Carbene Reaction Energetics for H₂ storage at 298K in kcal/mol to ± 1 kcal/mol

\[
\text{carbene} + \text{H}_2 \rightarrow \text{carbeneH}_2 \quad \Delta H = -14.9
\]
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. \( T \Delta S(298K) = +8.2 \text{ kcal/mol} \)

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

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

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

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

Carbene + H₂ → carbeneH₆ \( \Delta H = -8.6 \)
Adding H₂ to hydrogenate the double bond is exothermic by only 9 kcal/mol as compared to -31 kcal/mol for hydrogenation of C₂H₄.

CarbeneH₆ + H₂ → carbeneH₈ \( \Delta H = -32.6 \)
Adding H₂ to the hydrogenated carbene is quite exothermic – develop carbene reactivity scale.
Hydrogenation energies (kcal/mol) of carbenes

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$-\Delta H_{\text{rxn}}(298\text{K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbene + $\text{H}_2$ $\rightarrow$ carbeneH$_2$</td>
<td>14.9</td>
</tr>
<tr>
<td>carbeneH$_6$ + $\text{H}_2$ $\rightarrow$ carbeneH$_8$</td>
<td>32.6</td>
</tr>
<tr>
<td>$^1\text{CF}_2$ + $\text{H}_2$ $\rightarrow$ CF$_2$H$_2$</td>
<td>62.2</td>
</tr>
<tr>
<td>$^3$carbene + $\text{H}_2$ $\rightarrow$ carbeneH$_2$</td>
<td>101.3</td>
</tr>
<tr>
<td>$^3\text{CF}_2$ + $\text{H}_2$ $\rightarrow$ CF$_2$H$_2$</td>
<td>108.2</td>
</tr>
<tr>
<td>$^3\text{CH}_2$ + $\text{H}_2$ $\rightarrow$ CH$_4$</td>
<td>110.9</td>
</tr>
</tbody>
</table>
Heteroatom Organic Systems for Hydrogen Storage: The “Alabama Approach”

Other ways to release hydrogen from dihydroimidazoles, not previously known

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

Bo Arduengo
Hydrogen Production Using Ammonia-Borane

\[ \text{[H}_2\text{N-BH}_2\text{]}_n \xrightarrow{-\text{H}_2} \text{[HN=BH]}_n \xrightarrow{-\text{H}_2} \]

Linear polymer

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

Cyclic trimer ‘borazane’

\[ \text{H}_3\text{B-NH-NB-HH} \xrightarrow{-\text{H}_2} \text{HN-BN-NBH} \xrightarrow{-\text{H}_2} \]

Cyclic trimer ‘borazine’

‘diamondoid’

‘graphitic’

Collaborators: Fran Stephens & Tom Baker (LANL)
Reaction Energies in borane amines in kcal/mol @ 298K for chemical hydride storage

• Reaction energies for the sequential release of H$_2$ from borane amines (gas phase) based on the most accurate heats of formation now available – our calculated values.

\[
\begin{align*}
\text{BH}_3\text{NH}_3 & \rightarrow \text{BH}_2\text{NH}_2 + \text{H}_2 & \Delta H = -5.1 \\
\text{BH}_2\text{NH}_2 & \rightarrow \text{HBNH} + \text{H}_2 & \Delta H = 31.4 \\
\text{HBNH} & \rightarrow \text{BN} + \text{H}_2 & \Delta H = 134.3
\end{align*}
\]

• BH$_3$NH$_3$ will be a good source of H$_2$ as the release of H$_2$ from this species is not far from thermoneutral due to the donor-acceptor bond. Cannot make T too high as entropy also favors release of H$_2$.

• The reaction energies for forming BN/C$_2$ and BHNH/CHCH are ~ equal. Similarity of the isoelectronic C$_2$H$_{2m}$ and BNH$_{2m}$ systems except for m = 3. Due to differences in $\sigma$ bond energies.

• Can the salt [BH$_4^-$][NH$_4^+$] serve as an H$_2$ storage system? Estimate the lattice energy, $U_L$, of the salt from the empirical expression dependent on the volume.

\[
\begin{align*}
[\text{BH}_4^-][\text{NH}_4^+] (s) & \rightarrow \text{BH}_3\text{NH}_3(g) + \text{H}_2 & \Delta H(0K) = 0.2 \text{ kcal/mol} \\
[\text{BH}_4^-][\text{NH}_4^+] (s) & \rightarrow \text{BH}_3\text{NH}_3(s) + \text{H}_2 & \Delta H(0K) = -16.8 \text{ kcal/mol}
\end{align*}
\]

• We need to predict condensed phase interactions. Strong dipolar interactions.

### Bond Energies in kcal/mol for chemical hydride storage

<table>
<thead>
<tr>
<th>Reaction</th>
<th>B.E. (ΔH(0K))</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH₃-NH₃ → BH₃ + NH₃</td>
<td>25.9</td>
<td>dative</td>
</tr>
<tr>
<td>CH₃-CH₃ → 2 CH₃</td>
<td>87.9</td>
<td>C-C σ</td>
</tr>
<tr>
<td>BH₂=NH₂ → BH₂ + NH₂</td>
<td>139.6</td>
<td>B-N π + B-N σ</td>
</tr>
<tr>
<td>CH₂=CH₂ → 2 CH₂ (³B₁)</td>
<td>171.9</td>
<td>C-C π + C-C σ</td>
</tr>
<tr>
<td>BHNH → BH + NH</td>
<td>178.5</td>
<td></td>
</tr>
<tr>
<td>HCCH → 2 CH</td>
<td>228.1</td>
<td></td>
</tr>
</tbody>
</table>

- For C₂H₄, the C-C π bond is ~65 kcal/mol giving a C-C σ bond energy of 107 kcal/mol. Due to sp²–sp² bonding, not sp³-sp³ bonding.

- Estimate the B=N π bond energy by calculating the rotation barrier in BH₂NH₂
  
  Electronic contribution = 31.99 kcal/mol
  Zero point contribution = 2.02 kcal/mol
  Barrier at 0K = 30.0 kcal/mol

- Gives a very strong B-N single bond of 109.6 kcal/mol, comparable to the C-C σ bond. The high B-N σ + π bond energy in BH₂NH₂ is consistent with the fact that it does not release H₂ readily.
Energetics (kcal/mol) for the Release of H₂ (gas phase products)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (298K)</th>
<th>TS Energy</th>
<th>Bond Energy</th>
</tr>
</thead>
<tbody>
<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 → HAIIPH + H₂</td>
<td>34.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlIIPH → AlIP + H₂</td>
<td>45.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH₃NH₃ → BH₂NH₂ + H₂</td>
<td>-8.3</td>
<td>34.5</td>
<td>25.9</td>
</tr>
</tbody>
</table>

[BH₄⁻][PH₄⁺] (s) → BH₃PH₃ + H₂          | -13.2     |           |             |
[AlH₄⁻][NH₄⁺] (s) → AlH₃NH₃ + H₂         | -3.3      |           |             |
[AlH₄⁻][PH₄⁺] (s) → AlH₃PH₃ + H₂         | -9.3      |           |             |

- Isoelectronic species – no obvious advantage energetically and less capacity due to mass.
- Direct H₂ elimination above dative bond energy – need catalysts.
Reaction Pathway for $\text{H}_2$-Generation from $\text{BH}_3\text{NH}_3$ 

Relative energies in kcal/mol: 
Upper: B3LYP 
Middle: MP2 and CCSD(T)//MP2 
Lower: CCSD(T)//CCSD(T) using aug-cc-pVTZ basis set. 
ZPE: MP2/aug-cc-pVTZ 

B-N bond cleavage is energetically more favored over the unimolecular $\text{H}_2$ release from borane amine
Pathways for \( \text{H}_2 \)-Generation from BH\(_3\)NH\(_3\) + BH\(_3\)

**Rel. energies in kcal/mol:**

Upper:  B3LYP  
Middle:  MP2  
Lower:  CCSD(T)/MP2  
ZPE:  MP2/aVTZ  

\( \text{BH}_3 \) can serve as a catalyst for \( \text{H}_2 \) elimination from BH\(_3\)NH\(_3\).
Cyclization reaction energetics in the gas phase in kcal/mol

Highly accurate CCSD(T)/CBS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3\text{BH}_3\text{NH}_3 \rightarrow \text{c-(BH}_2\text{NH}_2\text{)}_3 + 3\text{H}_2$</td>
<td>-54.5</td>
</tr>
<tr>
<td>$\text{c-(BH}_2\text{NH}_2\text{)}_3 \rightarrow \text{c-(BHNH)}_3 + 3\text{H}_2$</td>
<td>-20.4</td>
</tr>
</tbody>
</table>

G3MP2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3\text{BH}_3\text{NH}_3 \rightarrow \text{c-(BH}_2\text{NH}_2\text{)}_3 + 3\text{H}_2$</td>
<td>-60.8</td>
</tr>
<tr>
<td>$\text{c-(BH}_2\text{NH}_2\text{)}_3 \rightarrow \text{c-(BHNH)}_3 + 3\text{H}_2$</td>
<td>-23.4</td>
</tr>
<tr>
<td>$3\text{BH}_3\text{PH}_3 \rightarrow \text{c-(BH}_2\text{PH}_2\text{)}_3 + 3\text{H}_2$</td>
<td>-49.1</td>
</tr>
<tr>
<td>$\text{c-(BH}_2\text{PH}_2\text{)}_3 \rightarrow \text{c-(BHPH)}_3 + 3\text{H}_2$</td>
<td>57.0</td>
</tr>
<tr>
<td>$3\text{AlH}_3\text{NH}_3 \rightarrow \text{c-(AlH}_2\text{NH}_2\text{)}_3 + 3\text{H}_2$</td>
<td>-83.6</td>
</tr>
<tr>
<td>$\text{c-(AlH}_2\text{NH}_2\text{)}_3 \rightarrow \text{c-(AlHNH)}_3 + 3\text{H}_2$</td>
<td>25.1</td>
</tr>
<tr>
<td>$3\text{AlH}_3\text{PH}_3 \rightarrow \text{c-(AlH}_2\text{PH}_2\text{)}_3 + 3\text{H}_2$</td>
<td>-64.7</td>
</tr>
<tr>
<td>$\text{c-(AlH}_2\text{PH}_2\text{)}_3 \rightarrow \text{c-(AlHPH)}_3 + 3\text{H}_2$</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.
Conclusions

• Electronic structure methods can be used to get highly accurate values of the thermodynamic properties of compounds related to fuels for combustion and hydrogen storage.

• Chemical hydrogen storage offers a significant opportunity for enabling the hydrogen economy as well as for SCRAMJet applications.

• We already have some potential materials – borane amines and carbenes as well as others (substituted NN compounds).

• We are designing affordable chemical materials and reactions that permit:
  – adequate hydrogen storage in terms of weight percent
  – acceptable stability until exposed to catalyst or activator
  – controlled evolution of hydrogen at usable pressure when catalyzed or activated
  – efficient (reasonable cost), safe regeneration