FLORIDA SOLAR ENERGY CENTER

Hydrogen Storage in Ammonia-Borane Complexes

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A Research institute of the University of Central Florida

Background

Amine Borane Complex

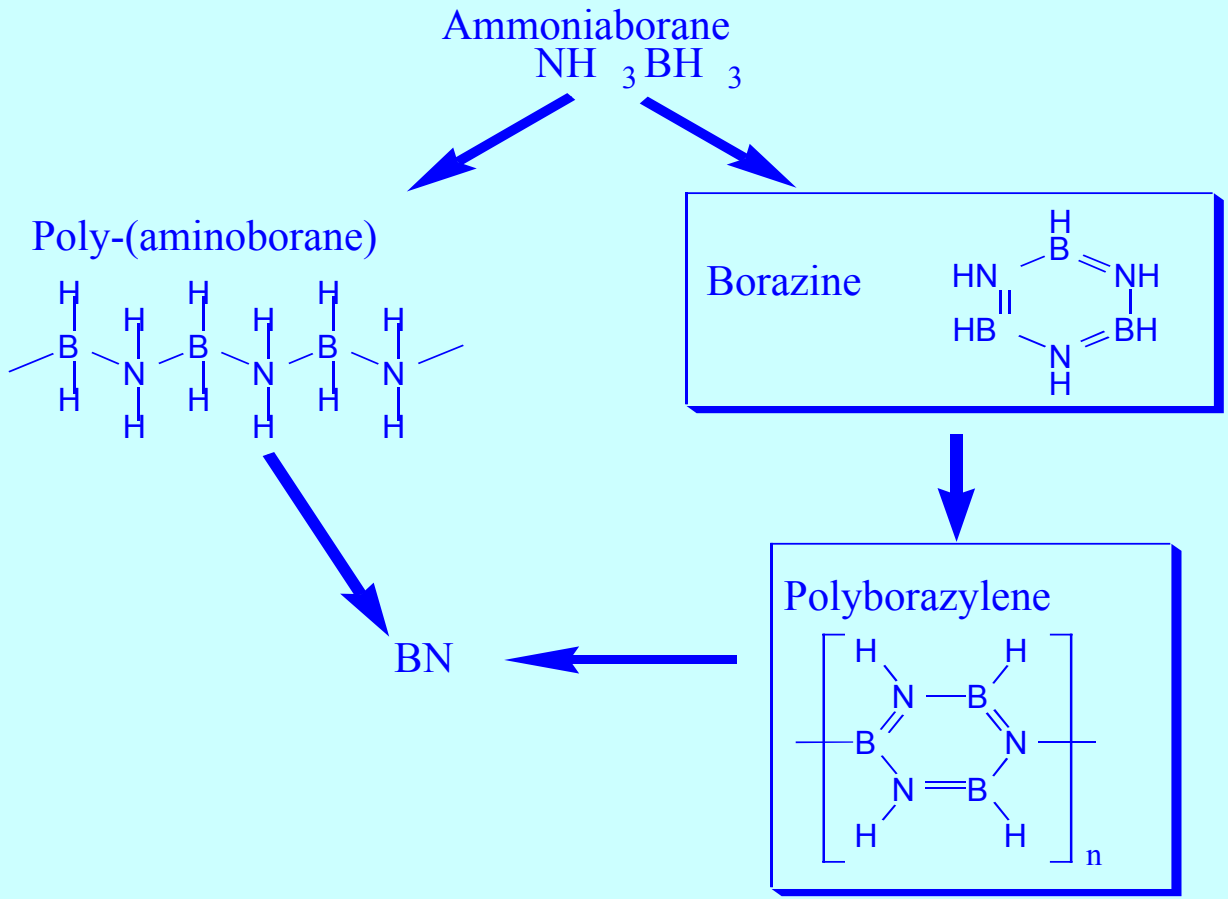
KNOWN:

- NH_3BH_3 (AB)$\rightarrow$ BN + $3H_2$ (20 wt% H_2)
  - Energy Density: 4.94 kWh/L for AB vs. 2.36 kWh/L for LH_2
- Begins hydrogen liberation at less than 140°C & 1 ATM
- AB is stable in air, water and many organic solvents
- Synthetic routes for preparing NH_3BH_3 are available

UNKNOWN:

- Regeneration (reversibility)

NH_3BH_3 Thermolysis

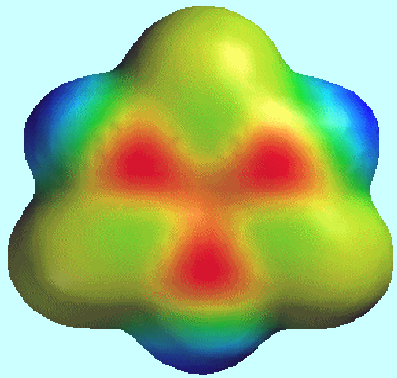


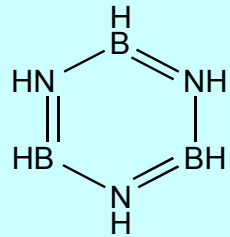
Our Approach

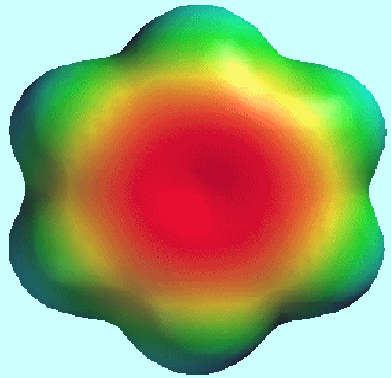
- **Borazine/Cyclotriborazane Cycle**
  - Cyclotriborazane decomposition to borazine: **6.47 wt%** hydrogen will be released
- **Polyborazylene Reduction**
  - Conversion of ammoniaborane complex to polyborazylene provides **~ 18 wt%** of hydrogen release

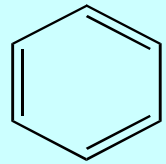
Borazine

- Borazine (mp –58°C and bp 53°C) is stable in gas phase up to 500°C
- Borazine is isoelectronic with benzene (*inorganic benzene)*
- Charge localisation on N makes borazine more susceptible to addition reactions and less stable than benzene

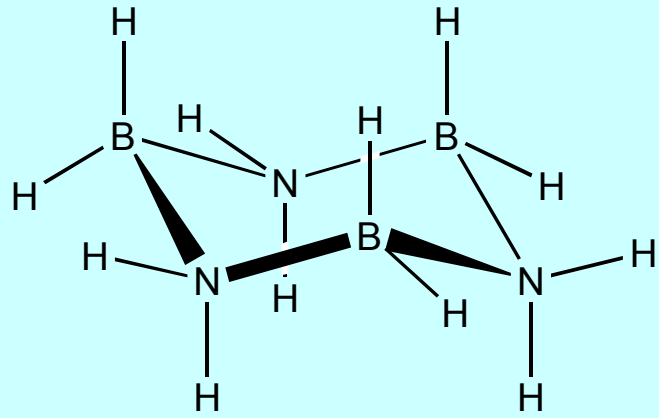








Cyclotriborazane



- Crystalline
- Not readily attacked by water
- Soluble in DMSO, ethers, NH_3, CH_3OH, dioxane

Ref: *Dahl, G. H.; Schaeffer, R. J. Am. Chem. Soc.* ***1961****, 83, 3032.*
Boddeker, K. W.; Shore, S. G.; Bunting, R. K. J. Am. Chem. Soc. ***1966****, 88, 4396.*
Shore, S. G.; Hickam, C. W. Inorg. Chem. ***1963****, 2, 638.*

Borazine/Cyclotriborazane Cycle

- How is borazine going to be converted to cyclotriborazane?
  - Direct Synthesis via Catalytic Hydrogenation
  - Indirect (Multi-Step) Synthesis
- What is the conversion efficiency of cyclotriborazane to borazine?

Borazine Hydrogenation

- **Reported failed attempt*:**
  - **Ni at 70 °C, 150 °C and 200 °C**
  - **Pd at 40-50 °C**
  - **Unidentified amorphous solid product**
- **Lower temperature catalyst is required**
- **Calculated Heat of Hydrogenation = 28.096 kcal/mol (Gaussian 03: *x86-Win32-G03RevB.01 3-Mar-2003; DFT B3LYP 6-31G*)**
- **Catalyst screening and molecular modeling are in progress**

***Wiberg, E.; Bolz, A. *Berichte der Deutschen Chemischen* 1940, 73B, 209.**

Indirect Synthesis

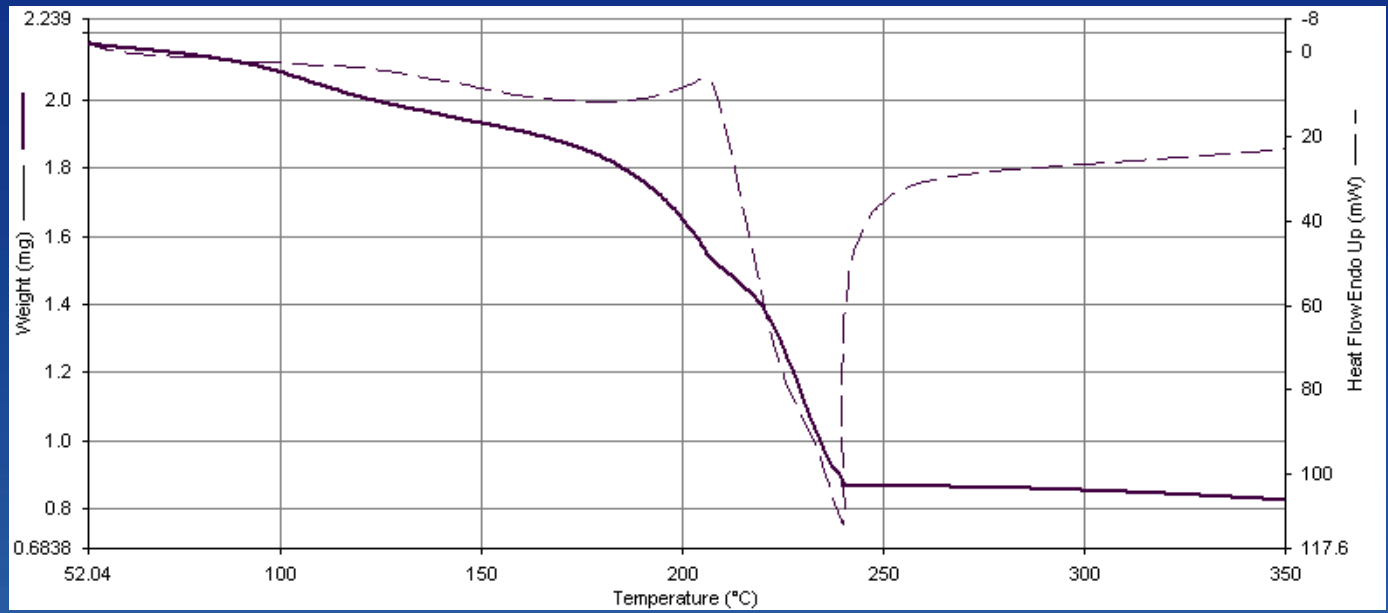
*$B_3N_3H_6 + 3HCl \rightarrow B_3N_3H_6.3HCl$

*$2B_3N_3H_6.3HCl + 6NaBH_4 \rightarrow 2B_3N_3H_{12} + 6NaCl + 3B_2H_6$

- 80% Yield
- Not easily purified
- Solid state reduction of $B_3N_3H_6.3HCl$ is under investigation

* Dahl, G. H.; Schaeffer, R. J. Am. Chem. Soc. **1961**, 83, 3032.

TG/DTA Analysis of Cyclotriborazane



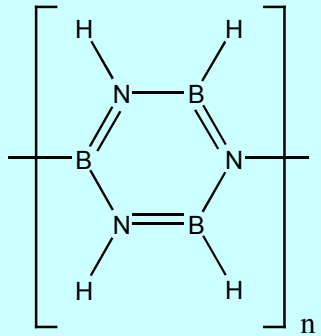
- Heating Rate: 40 °C/min
- ΔH = -1019 J/g
- Weight loss = 59% (Kinetic Related?)
- Prior work* reported 75% conversion to borazin and 100% H_2 release

* *Dahl, G. H.; Schaeffer, R. J. Am. Chem. Soc. 1961, 83, 3032.*

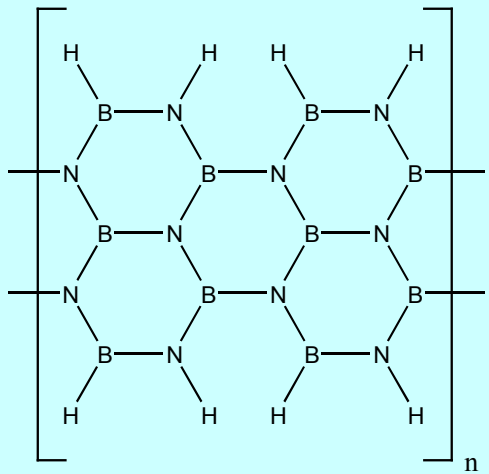
Polyborazylene

- Dehydrocoupling reaction of borazine
- A white moisture-sensitive solid
- Polyborazylene is a combination of linear (A), chain-branched, & fused cyclic segments (B)

(A)



(B)



Polyborazylene Reduction

PB + xHCl → PB.xHCl

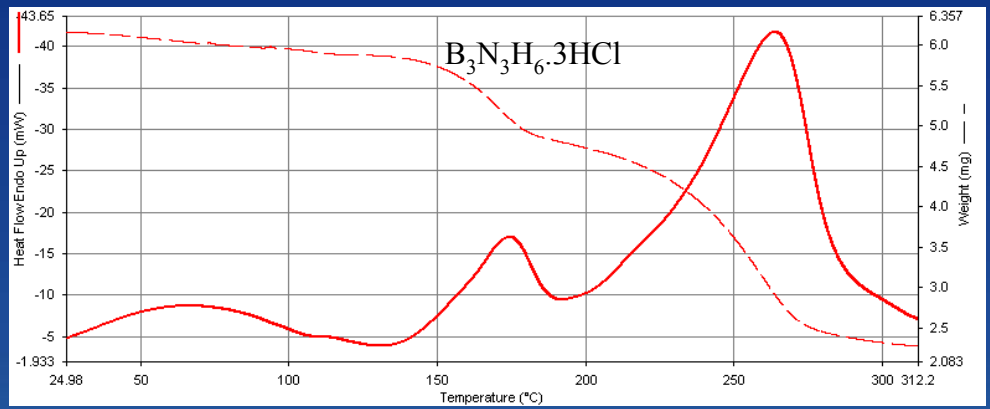
PB.xHCl + $NaBH_4$ → Hydrogenated PB

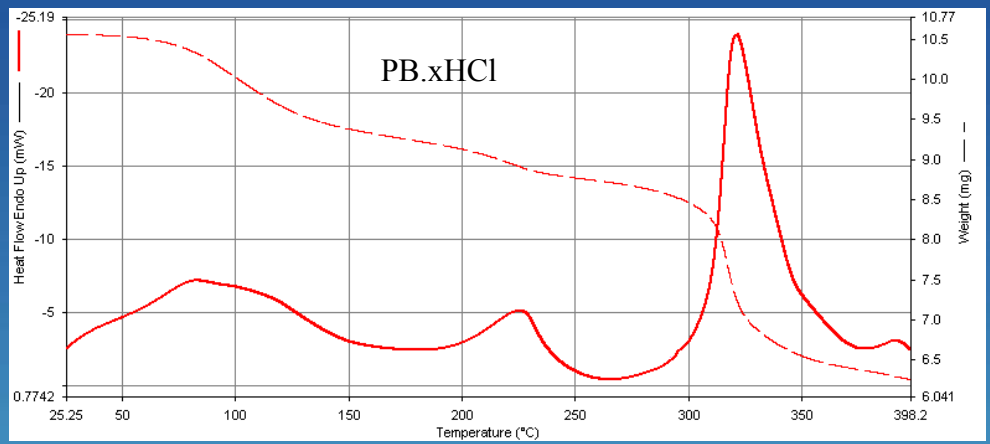
Advantage: solid↔solid for PB cycle
vs. Liquid↔solid for borazine

Is it possible?

PB + xHCl → PB.xHCl

- Based on the reported M_n = 1400 for PB, 250 mole of HCl per mole of PB was reacted!
- Similar characteristics in TG/DTA analysis between PB.xHCl and its analog $B_3N_3H_6.3HCl$
- Further characterization is underway





Summary

- Kinetic optimization for cyclotriborazane conversion to borazine
- Catalyst screening for borazine hydrogenation
- Alternative synthetic route for cyclotriborazane (solid state?)
- Polyborazylene reduction investigation
- 250 mole of HCl per mole of PB was reacted!
- Similar characteristics in TG/DTA analysis between PB.xHCl and its analog $B_3N_3H_6.3HCl$

Acknowledgment

National Aeronautics & Space Administration through Glenn Research Center.