

IV.B.4f Chemical Hydrogen Storage Using Polyhedral Borane Anion Salts

M. Frederick Hawthorne (Primary Contact) and Satish Jalisatgi

Department of Chemistry and Biochemistry
University of California, Los Angeles
607 Charles E. Young Drive East
Box 951569
Los Angeles, CA 90095-1569
Phone: (310) 825-7378; Fax: (310) 825-5490
E-mail: mfh@chem.ucla.edu

DOE Technology Development Manager:
Grace Ordaz

Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire

Phone: (303) 275-4795; Fax: (303) 275-4753
E-mail: James.Alkire@go.doe.gov

Contract Number: DE-FC36-05GO15058

Start Date: September, 2005

Projected End Date: September, 2009

Objectives

- Develop heterogeneous catalysts for the controlled generation of hydrogen from the hydrolysis of salts of $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{11}H_{14}^{-}$ ions.
- Determine the kinetics and mechanism of these catalyzed borane anion hydrolysis reactions to provide design data for large-scale hydrogen generation devices.
- Investigate blends of two or more anionic polyhedral borane salts of variable purity as commercially viable sources of hydrogen (analogous to hydrocarbon blends for optimized gasoline) with cost and performance as working parameters.
- Optimize existing processes for the conversion of diverse $>BH$ sources to $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$ for direct use in hydrogen generation without extensive purification.

Approach

Borohydride compounds offer the potential for significant hydrogen storage capacity, but most work to date has focused on one particular anion, BH_4^- , which requires high pH for stability and large energy costs for regeneration. Other borohydride compounds, in

particular polyborane anions, may offer comparable hydrogen storage capacity without requiring high pH media and with significantly reduced energy costs for regeneration.

The UCLA project will provide the overall program focal point for the investigation of polyhedral borane anions $B_nH_n^{2-}$ ($n = 10$ and 12), $B_{11}H_{14}^{-}$ and their derivatives as reservoirs for stored electrons available for hydrogen release upon catalyzed hydrolysis; as substitute for electrochemical studies leading to reversible electron storage, and as reactants in reversible hydrogen storage.

Results

1. Conversion of Et_4NBH_4 to $Closo-B_{10}H_{10}^{2-}$ and $Closo-B_{12}H_{12}^{2-}$ ions by thermolysis.
2. Synthesis of $NaB_{11}H_{14}^{-}$. The synthesis was optimized by reacting $B_{10}H_{14}$ with $NaBH_4$ at an elevated temperature.
3. Catalytic hydrolysis of $NaB_{11}H_{14}^{-}$, $Closo-B_{10}H_{10}^{2-}$ and $Closo-B_{12}H_{12}^{2-}$.

Various metal catalysts were investigated for the hydrolysis of $B_{11}H_{14}^{-}$, $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ anion salts. In each case the rate of hydrogen release depends upon the following variables:

- Choice of metal catalyst
- Temperature
- Concentration of the catalyst
- pH of the reaction mixture
- Choice of cation for polyhedral borane salt

Rate of reaction and efficiency can be measured by ^{11}B nuclear magnetic resonance of the reaction mixtures or by hydrogen evolution as a function of time.

Transition metal ions, such as cobalt, nickel, palladium and rhodium are known to form metal borides in the presence of reactive borane species. Transition metal borides are good first choice catalysts since transition metal ion borane hydrolysis catalysts would most likely be converted to the respective borides during the hydrolysis reactions. This complicating possibility is removed by purposely employing transition metal borides as exploratory catalysts that are inert to modification by reaction with borane species present. For purposes of initial exploration, rhodium boride, nickel boride and cobalt boride were examined for their catalytic activity in the hydrolysis of $NaB_{11}H_{14}^{-}$, $(NH_4)_2B_{12}H_{12}$, $K_2B_{12}H_{12}$ and $K_2B_{10}H_{10}$.

Below is a summary of the catalyzed hydrolysis of polyhedral anions investigated:

Polyhedral boranes	Weight of salt	Water consumed (mg)	RhB catalyst (mg)	System wt. (mg)	T (°C)	pH	Relative rate ($\times 10^{-3} \text{ min}^{-1}$)	H ₂ released mmol wt%*	
NaB ₁₁ H ₁₄	70.2 mg (0.450 mmol)	279.0	4.7 (5.0 mol%)	354.7	80	2	0.1	10.9	6.15
K ₂ B ₁₀ H ₁₀	88.4 mg (0.450 mmol)	261.0	4.7 (5.0 mol%)	354.7	80	6	8.3	9.6	5.41
(NH ₄) ₂ B ₁₂ H ₁₂	80.1 mg (0.450 mmol)	311.0	4.7 (5.0 mol%)	396.7	80	1	11	11.4	5.74
(NH ₄) ₂ B ₁₂ H ₁₂	80.1 mg (0.450 mmol)	311.0	4.7 (5.0 mol%)	396.7	90	1	22	11.4	5.74
(NH ₄) ₂ B ₁₂ H ₁₂	80.1 mg (0.450 mmol)	311.0	2.3 (2.5 mol%)	394.3	90	1	8.3	11.4	5.78

The calculations are based upon water consumed.

System wt: wt of boranes + water consumed + catalyst

*Hydrogen wt%: wt of H₂/wt (boranes + water + catalyst) x 100

DOE targets for hydrogen storage wt% for 2005: 4.5%; 2010: 6.0%; 2015: 9.0%

- Of the three boride catalysts investigated, only rhodium boride was able to catalyze the hydrolysis of the generally inert B₁₂H₁₂²⁻ and B₁₀H₁₀²⁻ ions. These ions were inert to nickel boride and cobalt boride catalysts.
- Hydrolysis of NaB₁₁H₁₄ was faster than any B₁₂H₁₂²⁻ and B₁₀H₁₀²⁻ salts investigated and proceeded in the presence of all three boride catalysts. The hydrolysis rate was faster with rhodium boride compared to nickel and cobalt borides.
- Choice of cation can affect the rate of hydrolysis; (NH₄)₂B₁₂H₁₂ hydrolysis is faster than K₂B₁₂H₁₂ using the rhodium boride catalyst.
- Both temperature and pH affect the rate of hydrolysis of all polyhedral borane ions under investigation. Additional studies are required to determine the mechanistic meaning and usefulness of the pH effects and their applications in large scale hydrogen generation.
- All hydrolysis reactions proceed to completion giving quantitative hydrogen and boric acid production.

Future Plans

- Investigate alternative transition metal boride catalysts.
- Identify and characterize rhodium boride catalyst useful for B₁₁H₁₄⁻, B₁₂H₁₂²⁻, and B₁₀H₁₀²⁻ anion hydrolyses.
- Study the kinetics of the reaction; effect of pH, cation identity and ionic strength; determination of activation parameters; determine the reaction mechanisms.
- Examine B₁₂X₁₂²⁻ (X = Cl, CH₃, OR) in catalyzed hydrolysis reactions and the mechanistic implications of these results.
- Identify appropriate polyhedral borane-amine complexes and ammonium salts for catalytic dehydrogenation studies (with Center).

FY 2006 Publications/Presentations

1. Merit review presented at DOE Chemical hydrogen storage meeting held at Washington, DC, May 2006.