

PNNL Progress as Part of the Chemical Hydrogen Storage Center of Excellence

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Project
ST_18_Autrey

Overview

Timeline

- Start 3/2005
- End 3/2010
- 85% Complete

Budget

- FY08: \$2400K
- FY09: \$2350K

Barriers Addressed

- Volumetric Density
- Gravimetric Density
- Hydrogen Release Rate
- Fuel Cost
- Fuel Cycle Energy Efficiency
- Hydrogen Purity

Collaborations



Relevance

- **Objectives**

- Develop materials & methods for low temperature (<85 °C) release of pure hydrogen (99.99%) from chemical hydrides that can achieve DOE targets (>90g H₂/kg and >70g H₂/l)

- **Focus on quantitative measurements of impurities in H₂.**

- Develop high efficiency methods for large scale synthesis of chemical hydrogen storage materials

- **Fabricate reactor to prepare bench scale quantities of ammonia borane.**

- Develop high efficiency off-board methods for chemical hydride regeneration to achieve DOE targets (60%)

- **Coordinate with ANL to do preliminary efficiency analysis of regen process.**

- Support collaborators through expertise in chemistry & characterization to determine the kinetics & thermodynamics of hydrogen release and regeneration of H-storage materials

- **Work with Center partners to characterize materials and novel approaches to store and release hydrogen.**

- **Impact** Increased assessment of materials and approaches designed to specifically address DOE barriers (volumetric & gravimetric density, H-release rates at low temperatures, H₂ purity, fuel cost and fuel cycle energy efficiency)

Approach

- **Solid State Chemical Hydrogen Storage**

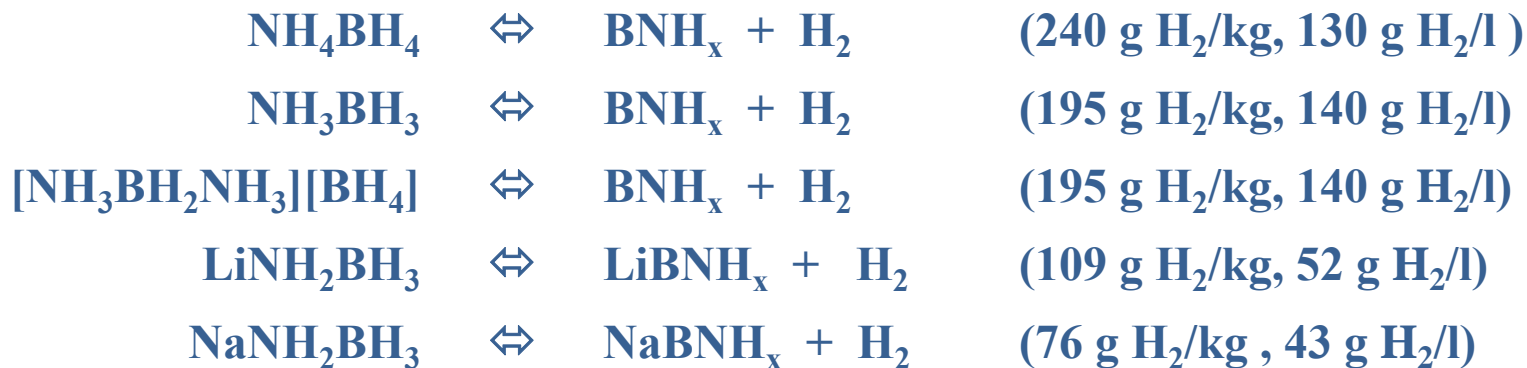
- Combine experimental & computational approaches to develop a mechanistic understanding of H-release from amine boranes and their regeneration from spent fuels.

A comprehensive understanding will enable the development of rational approaches to enhance rates of release, increase purity of hydrogen, and provide energy efficient regeneration schemes.









Approach

- Kinetics and thermodynamic property measurements for hydrogen release and regeneration of spent fuels
- Experimental: NMR and Raman Spectroscopy, XRD, TG/DSC/MS, PCI, Volumetric analysis. Mass spec, NMR, IR, and titration to determine and quantify impurities
- Computational: Electronic structure theory (DFT, MP2 & G3) to understand structural relationships and continuum solvation models to understand solvation effects

Solid phase chemical hydrogen storage materials studied



Accomplishments: Milestones FY09

Q3		Determine mechanism for second equivalent of hydrogen from ammonia borane. Based on mechanism, suggest list of potential approaches to enhance kinetics.
Q4		Complete assessment of the impact of fuel element dimension on global hydrogen release kinetics from monolithic AB.
Q4		Complete assessment of ammonium borohydride stability (minimum duration of 7 days), and make a go-no go decision on further investigation of ABH ₂ as a hydrogen storage material.
Q4		Complete synthesis and characterization of Co-H regeneration materials and demonstrate >50% efficiency for regeneration at bench scale (integrated batch processes)
Q4		Expand theory investigation on organometallic hydrides and develop a prioritized list for experimental investigation in the regeneration task
Q1		Deliver gap analysis, scope and schedule (to meet DOE MYPP) for regeneration engineering to the Center and DOE as part of Phase 2 planning activities
Q4		Submit a minimum of 1 joint publication from the IPHE activities with the UK, China, New Zealand, and the US
Q3		Determine mechanism for hydrogen from Li-AB. Based on mechanism, suggest additional promising AB-MH materials for study.

Accomplishments

Significant PNNL Accomplishments this year

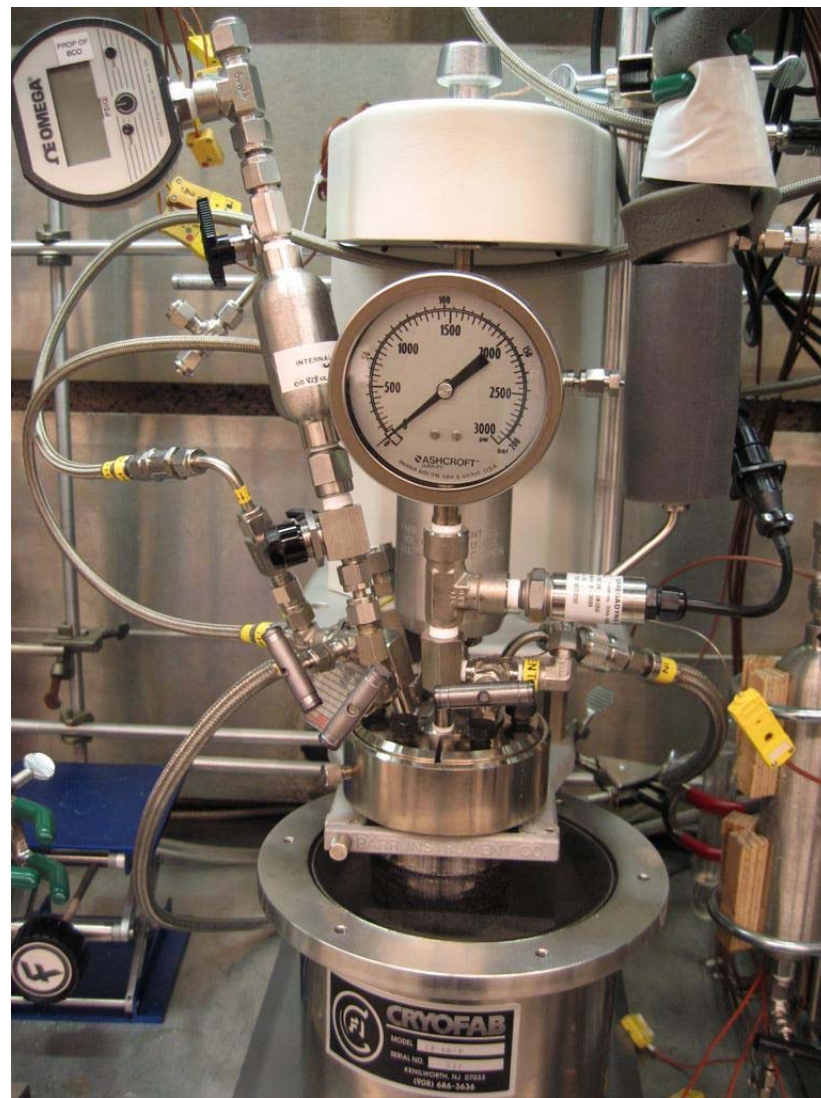
- *Scaled up AB synthesis (one-pot >95% yield, >99% purity)*
- *Determined stability of solution phase AB (to compare with solids)*
- *Quantified impurities in H₂ from AB and initiated approaches to mitigate and control*
- *Optimized anti-foaming agents to retain solid state AB fuel morphology*
- *Expanded studies of M-NH₂-BH₃. mechanisms of H₂ release, rates, stability studies, impurities (IPHE collaboration)*
- *Developed approach to stabilize NH₄BH₄ at room temperature*
- *Demonstrated hydride transfer chemistry from 'activated' H₂ to digested fuels using non-precious metal reagents*
- *9 peer-reviewed publications*

Accomplishments: Scale-up First Fill Ammonia Borane

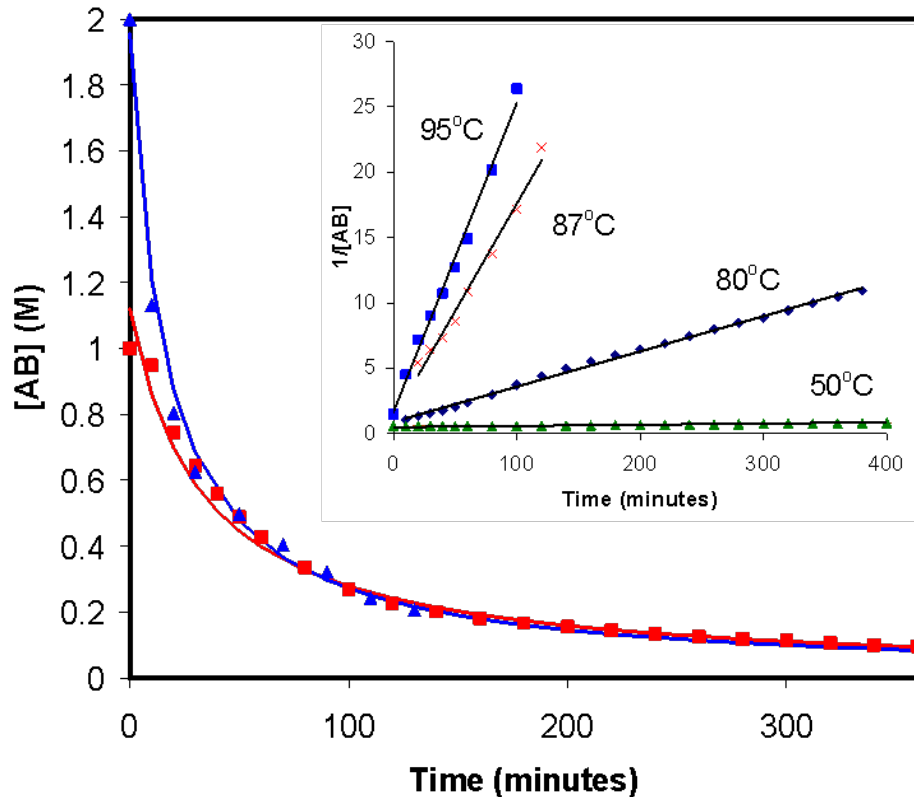
- ▶ One-pot batch reactor
 - Quantitative (isolated yields ~98%)
 - Purity (^{11}B NMR ~99%)
 - 2-10 gram batch reactor
 - $\text{NaBH}_4 + \text{NH}_4\text{X}$ in liq. NH_3 , THF
 - 150 psi, ambient temperature
 - THF and NH_3 can be recycled

Components for system to prepare 100 g batch material on bench top. Can be further scaled.

R/H performing cost analysis to compare with Purdue and OSU processes.



Accomplishments: Stability of AB (in solution) – relevance to regen and 1st fill

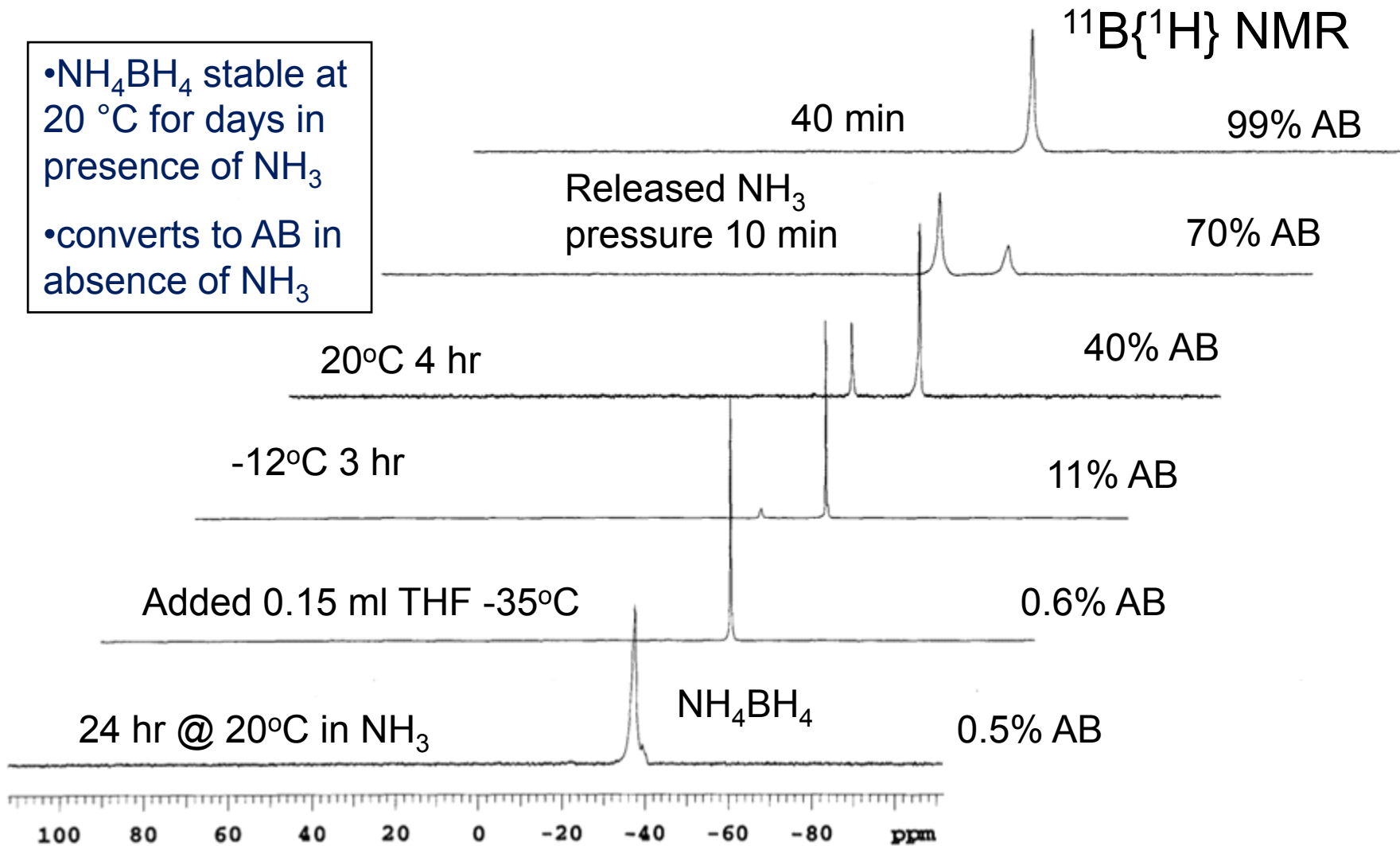


- Solid state AB meets stability targets.
- In solution AB decomposition is 2nd order.
- Short shelf life (days at room temperature) for concentrated AB solutions
- AB stability is solvent dependent; need lower concentrations or stabilizers.

Barriers and rates define stability of concentrated solutions to set engineering limits for H-release and regeneration.

Accomplishments: Stabilization of ammonium borohydride at room temperature (destabilize to make AB)

- NH_4BH_4 stable at 20 °C for days in presence of NH_3
- converts to AB in absence of NH_3



NH_4BH_4 shown for the first time to be stable at room temperature.

Accomplishments: Anti-foaming agents for solid ammonia borane

- ▶ Solid AB foams significantly with release of 1st eq H₂
- ▶ Explored over 30 different additives



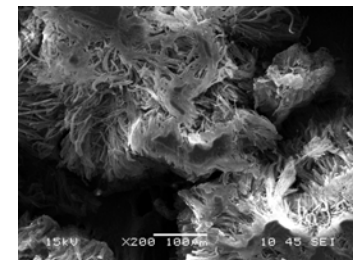
15wt% MC/AB

15wt% MC/AB heated to 180 °C

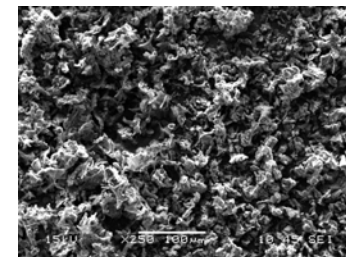
10wt% MC/AB heated to 180 °C

15wt% MC/AB (T2) heated to 180°C

Neat AB heated to 180°C



SEM images of MC/AB before (above) and after (below) heating to 180 °C (loss of 2.5 eq of H₂ (13 wt% H₂))



Best case: 10-20 wt% of methyl cellulose (MC) prevents foaming with proper preparation. 100 mg AB > 100 ml H₂.

Accomplishments: Mechanistic studies of metal amido boranes (IPHE* project) to modify thermodynamics and kinetics

▶ Decomposition

■ In solid state (2 distinct steps)

- $2\text{LiAB} \rightarrow \text{Li PAB} + \text{hydrogen}$
- $\text{Li PAB} \rightarrow \text{'lithium polyborazylene'} + \text{hydrogen}$
- Rate has very steep temperature dependence

■ In solution (two steps coupled)

- $\text{LiAB} \rightarrow \text{'lithium polyborazylene'} + \text{hydrogen}$

▶ All materials (to date) are found to be exothermic H-release

▶ Relative rates $\text{NaNH}_2\text{BH}_3 > \text{LiNH}_2\text{BH}_3 > \text{NaNH}(\text{Me})\text{BH}_3 > \text{KNH}(\text{tBu})\text{BH}_3$

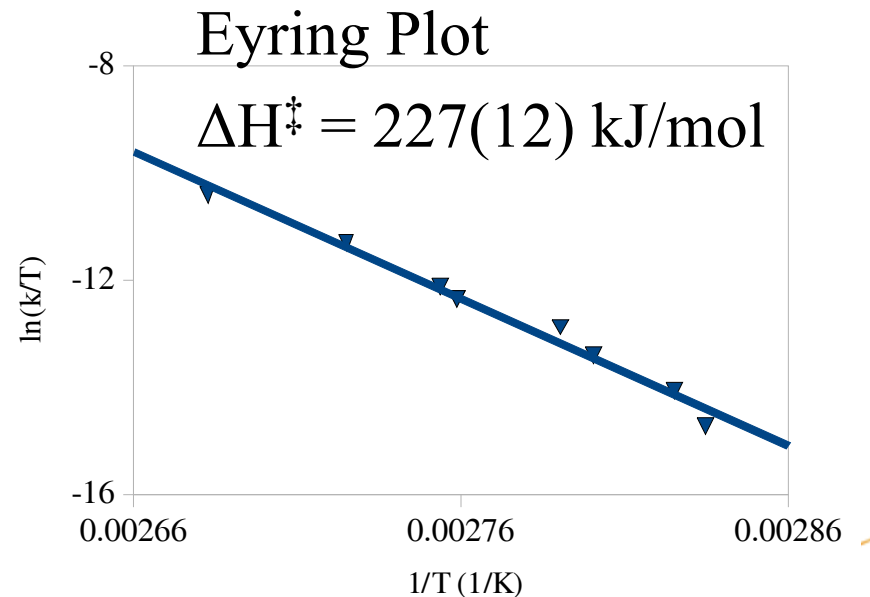
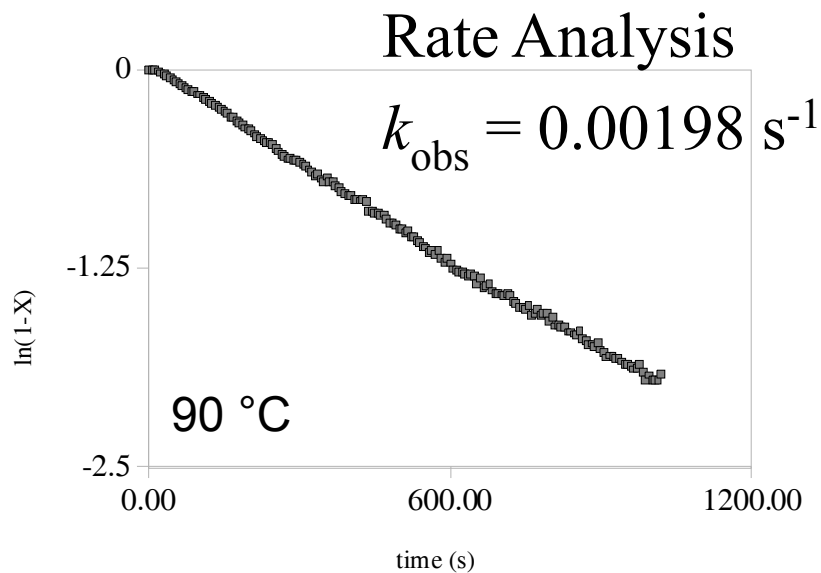
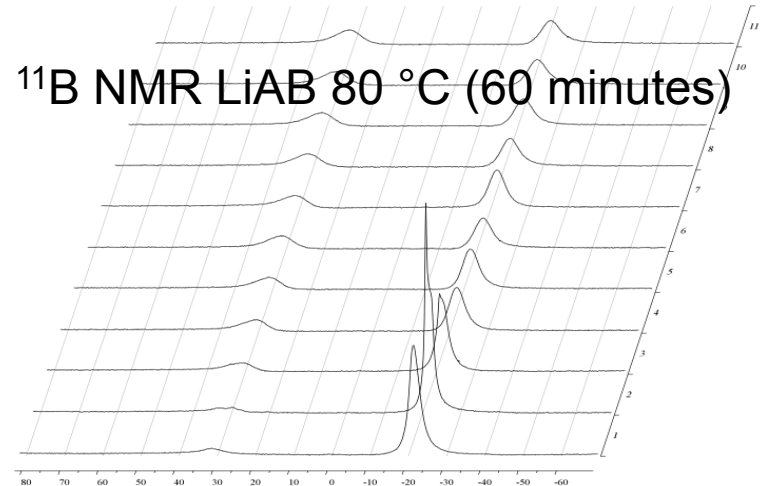
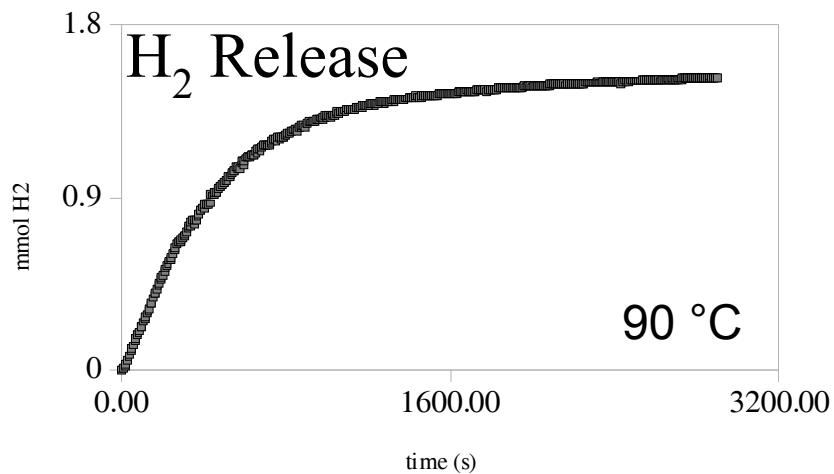
NaAB fastest but not as stable as LiAB at lower temperatures



*International Partnership for Hydrogen Economy Project:
PNNL, Dalian, RAL, Oxford, IRL, LANL



Accomplishments: Solid LiAB releases H₂ at lower temperatures yet more is stable than AB



LiAB appears more stable than AB under storage conditions and more reactive under release conditions

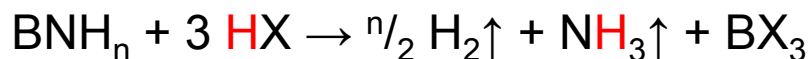
Accomplishments: Quantify impurities in H₂ from decomposition of solid AB

- ▶ What is the yield of borazine (reported to be the major volatile impurity in AB decomposition). Does borazine yield increase with increasing ramp rate?
 - **No, Independent!** 4±2 wt% (¹¹B NMR) w/release of 15 wt% H₂
- ▶ What is the yield of NH₃ from decomposition of solid AB?
 - Measured between 100-200 ppm (Draeger tubes)
 - Mass Spec data with Dedrick and Behrens (SNL) gives insight into mechanism of formation
- ▶ Does LiNH₂BH₃ provide approach to increase H₂ purity?
 - No borazine
 - ~2000 ppm NH₃ (1 eq H₂)

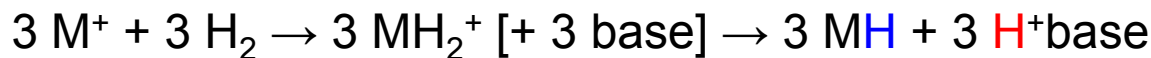


Approach: Regeneration of AB guided by theory, experiment & engineering analyses

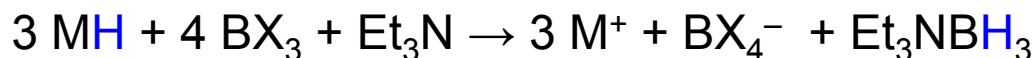
1. Digestion



2. Transition Metal Hydride Formation



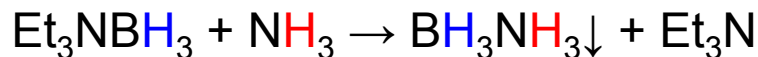
3. Hydride Transfer/Ligand Redistribution



4. Recycle



5. Ammoniation

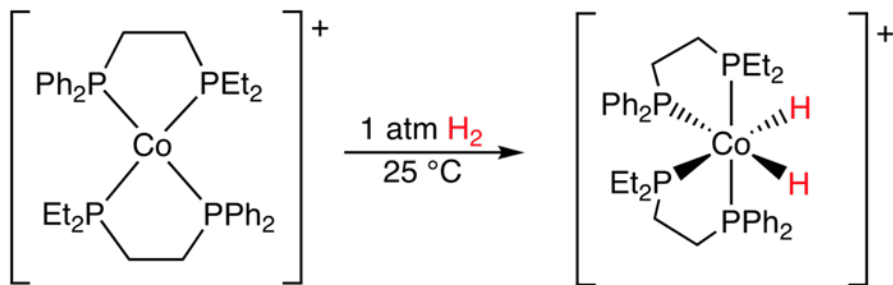


Goals:

MH₂ and HX have similar pK_as to optimize efficiency (i.e., integrate common base in steps 2 & 4).

H- donor ability is matched to H- acceptor ability of BX₃.

Accomplishments: Heterolytic H₂ activation and hydride formation by a cobalt complex (step 2)

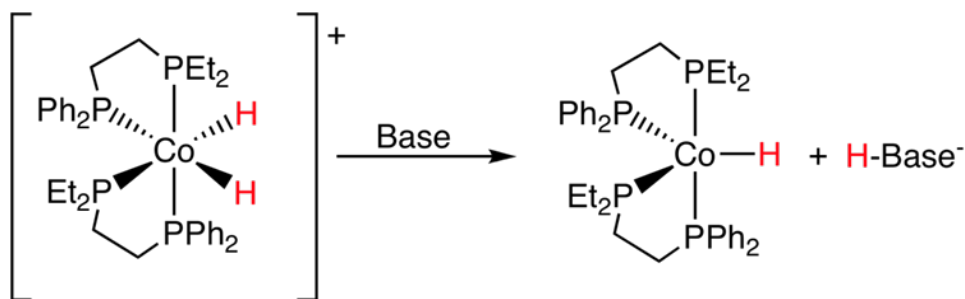


(dedpe)₂Co⁺

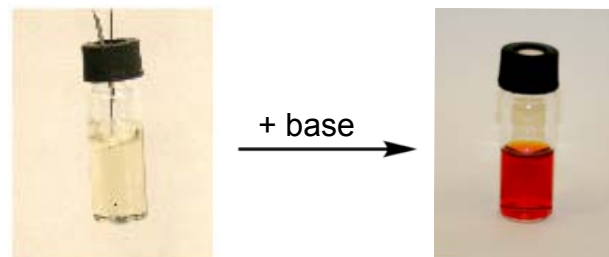
The blue cobalt complex reacts with 1 atm of H₂ gas within seconds at room temperature.



Cobalt hydride formation



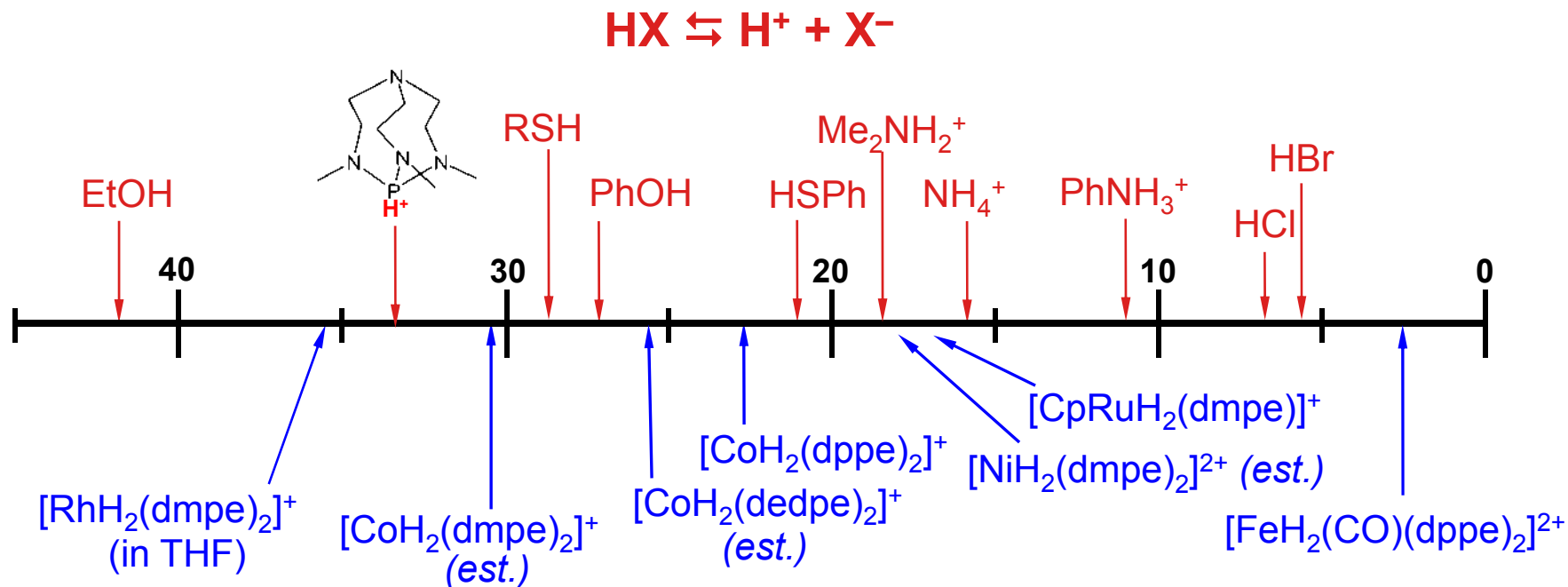
Base promotes the formation of the reactive monohydride complex.



Demonstrated activation of H₂ at ambient temperature and pressure with Cobalt.

Accomplishments: expanded pKa scale for L₂MH₂ & HX to predict hydride formation reaction (step 2)

MH₂ complexes to right of HX are deprotonated by X⁻.



dmpe: Me₂PCH₂CH₂PMe₂
 dppe: Ph₂PCH₂CH₂PPh₂
 dedpe: Ph₂PCH₂CH₂PEt₂



Prepared new cobalt dihydrides, estimated pK_as to determine match with literature values of bases (X⁻).

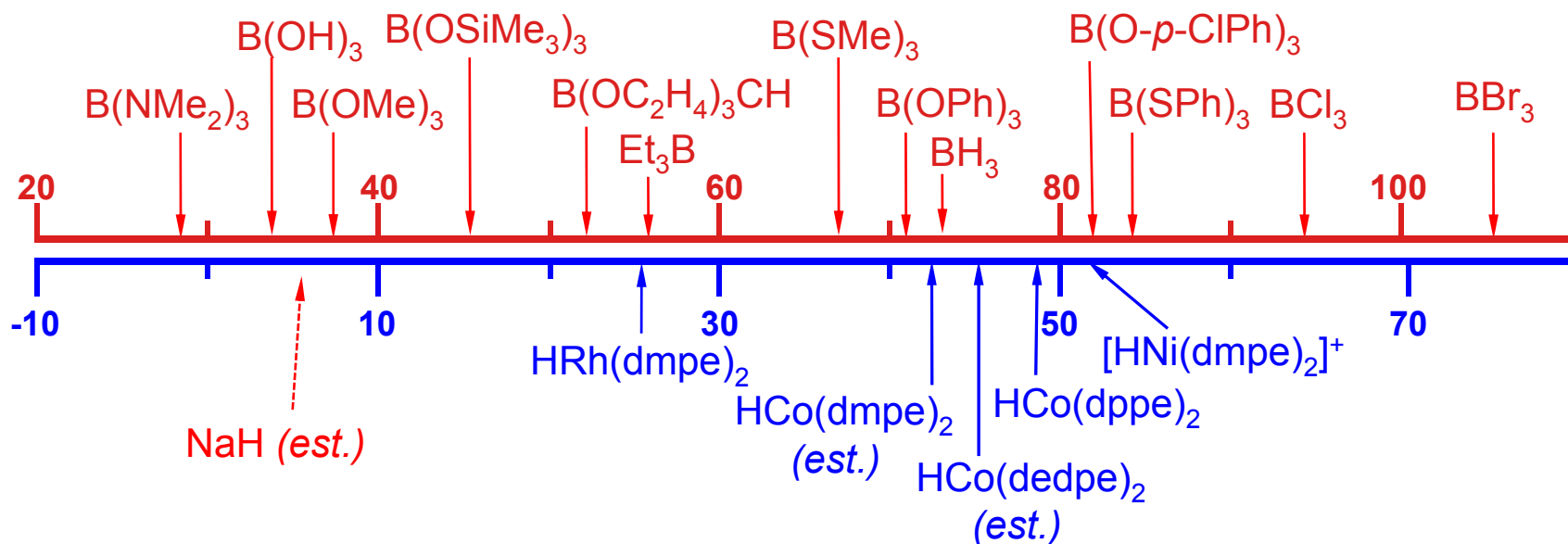
Accomplishments: expanded thermodynamic scale to predict hydride transfer reactions (step 3)

BX₃ compounds to right of L₂MH accept H⁻ from that complex.

Hydride Affinity (-ΔH): BX₃ + H⁻ → HBX₃⁻

(gas-phase calculation)

Not all B-O bonds
are the same!

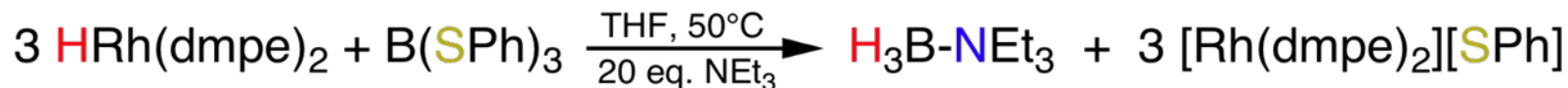


Hydride Donor Abilities (ΔG): HML₂ → ML₂⁺ + H⁻

(measured in acetonitrile)

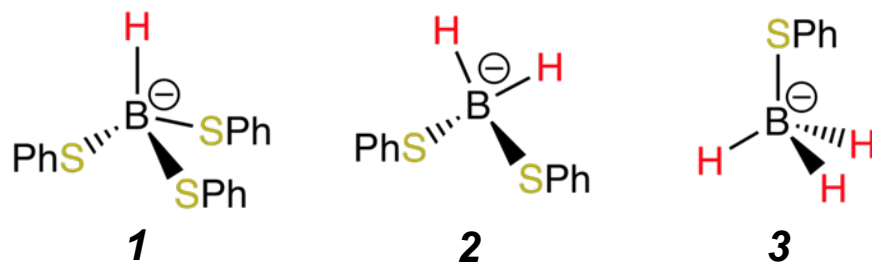
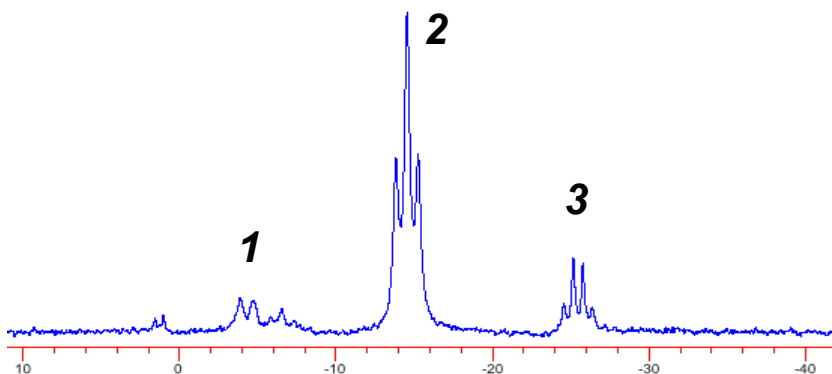
Scales show match between H⁻ acceptor ability of digested fuel targets (BX₃) and H⁻ donating ability of new TM hydrides.

Accomplishments: Production of Et₃NBH₃ from TM hydride demonstrated (steps 3 & 4)

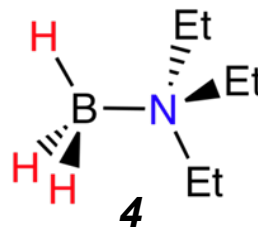
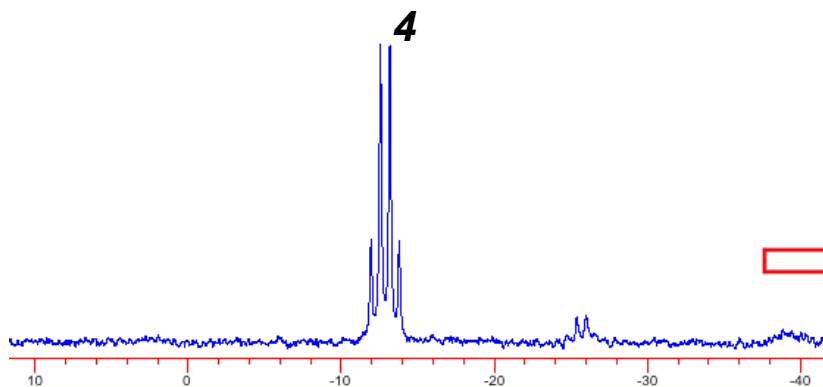


Proton coupled ¹¹B NMR data:

Initially, several B-H species are observed.

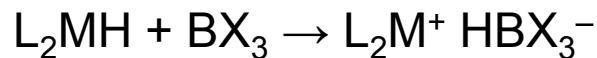


Multiple hydride transfers and facile ligand redistribution result in nearly complete formation of H₃B-NEt₃ after mild heating.

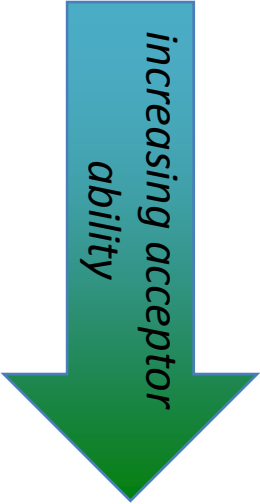


Demonstrated activation of H₂ (with Rh) and conversion of B(SPh)₃ to borane at moderate temperature.

Accomplishments: Series of digested fuel targets (BX₃) tested to accept hydride (H⁻) from (diphosphine)₂MH complexes



decreasing donor ability

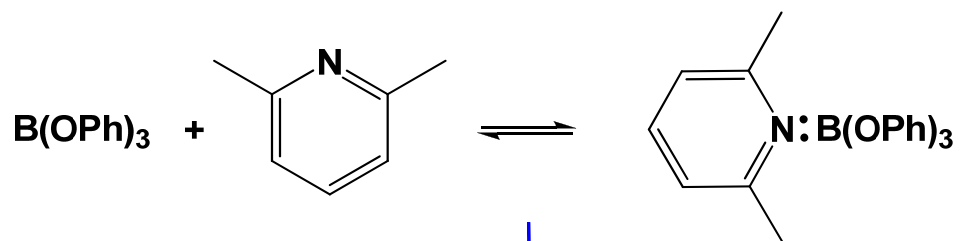
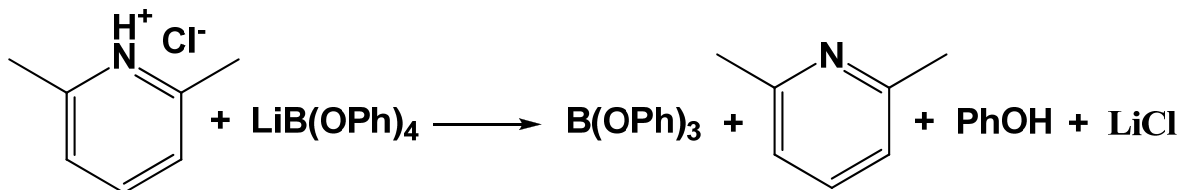



BX ₃	Rh dmpe	Co dmpe	Co dedpe
(<i>t</i> -BuO) ₃ B	✗		
C ₆ H ₄ S ₂ BH	✓		
(PhO) ₃ B	✓	✗	
(PhS) ₃ B	✓	✓	✓
(C ₆ F ₅ O) ₃ B	✓	✓	
BCl ₃	✓		

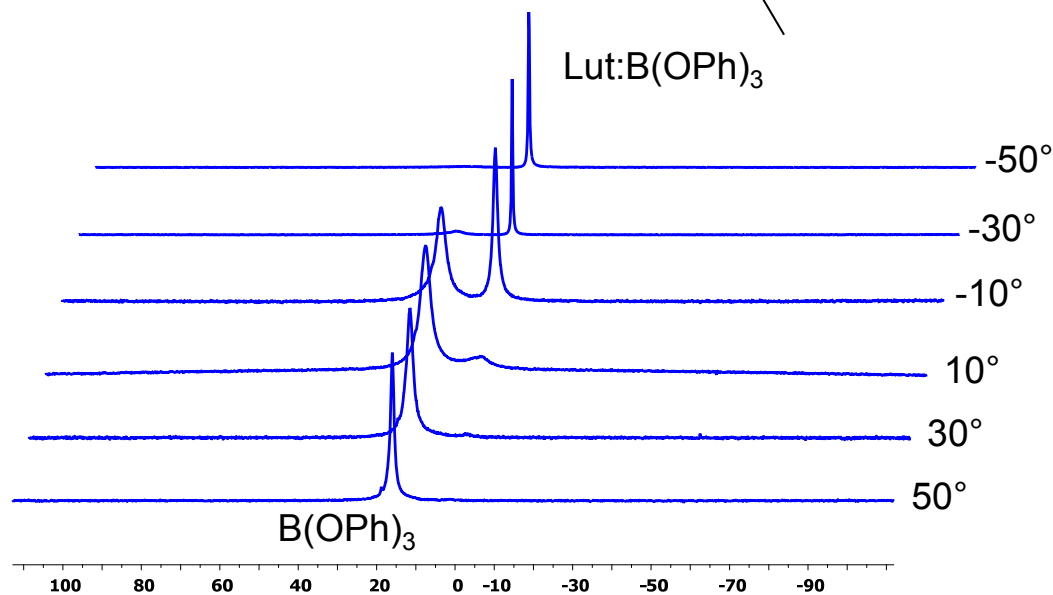
dmpe: Me₂PCH₂CH₂PMe₂
dedpe: Ph₂PCH₂CH₂PET₂

Preparation and testing of cobalt complexes and BX₃ compounds is under way.

Accomplishments: Recycle of $B(OPh)_4^-$ demonstrated (step 4)



$\Delta H^\circ = -0.26 \text{ kcal/mol}$
 $\Delta S^\circ = +1.9 \text{ cal/mol}$

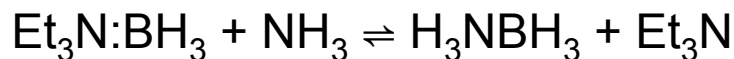


*Acids with $pK_a \geq PhOH$
cleave $B-OPh$ bond.*

*Hindered amine = weak $B-N$
bond.*

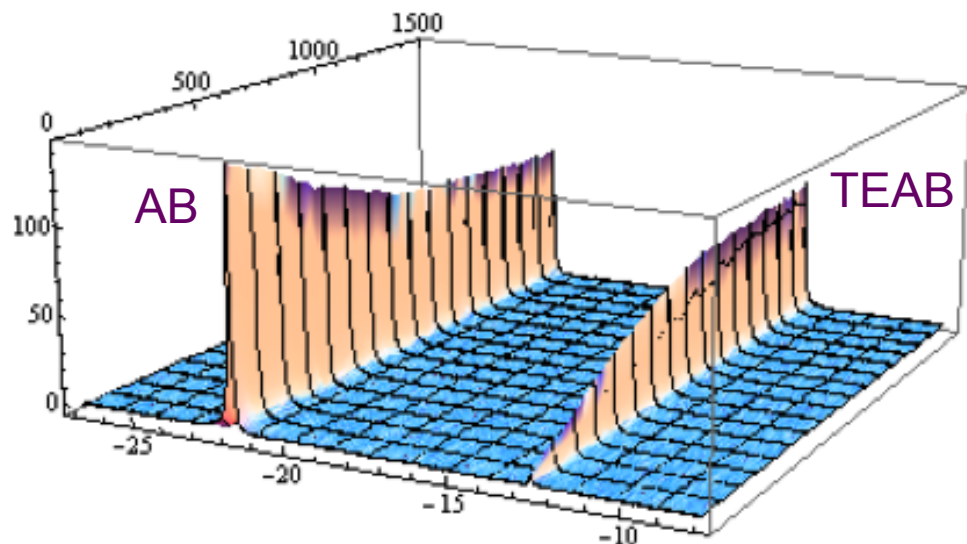
Accomplishments: Equilibrium and rate parameters determined for ammoniation of triethylamine: BH_3 (step 5)

$$K = 2.7$$

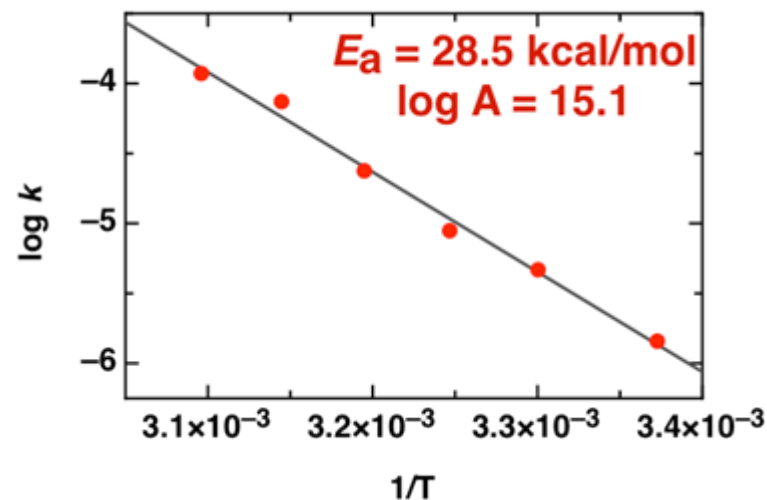


Time dependence of ^{11}B NMR spectrum for reverse reaction

Initial conditions: 0.29 M TEA, 0.08 M AB in THF, 45 °C



	expt	calc
$\Delta_r G^\circ$	-0.7	-0.2
ΔG^\ddagger	27	28



Favorable equilibrium, 2nd order kinetics, strong dependence of rate on T ... AB can be recovered from product mixture.

Summary

Release ...*focus on stability, solid fuel forms and H₂ purity*

- Stability of AB and NH₄BH₄ ... short shelf life AB in solution. NH₄BH₄ stable at room temperature
- Additives... fibrous compounds preserve solid fuel morphology)
- Purity of H₂ ... ammonia (100-200 ppm) and borazine (~4wt%) independent of heating rate
- Metal amido boranes (LiAB) ... high rates at low temperatures but stable at moderate temperatures

First fill AB Scale up

- Batch reactor to prepare AB (98/99). Minimize separations
- 10 g scale demonstrated, 100 g scale reactor next

Summary

Regeneration ... *developed a process for regenerating AB from H_2 and demonstrated individual steps.*

- Demonstrated H_2 activation with cobalt complex and conversion to $(\text{diphos})_2\text{CoH}$ with base
- Demonstrated H^- transfer to digested fuel targets (BX_3) from $(\text{diphos})_2\text{CoH}$... readily generated with H_2 and base
- Collaborated with ANL to obtain preliminary estimate of energy efficiency for approaches that digest spent fuel to B(OPh)_3 and NH_3 .
 - Convert residual B-H to H_2 .
 - Preserve residual B-H bonds in $(\text{BHNH})_n$.
 - Preliminary estimate of well-to-tank efficiency is 25-47%.
 - Base and transition metal complex undefined.
 - Energy for separations in recycle of B(OPh)_4^- not included.
 - Approach that preserves residual B-H is ~10% more efficient.

Collaborative Activities

Chemical Hydrogen Storage Center of Excellence

- UCD - study AB on nanoBN
- Penn - NMR and calorimetry support to Penn
- UW - measure ΔH for catalytic AB
- UO - measure ΔH for CBN compounds
- R&H - develop cost est. for 1st fill & regen
- Alabama - develop solvation models & benchmarking thermochemistry
- USB - characterize novel BX_3 esters

IPHE

- DICP, IRL, RAL, Oxford, LANL - study properties of metal amido boranes

Independent Projects

- H2 Tech - best practices for chemical hydrides

Materials 'Reactivity' Program

- Dedrick (SNL) and Anton (SRNL) - understand reactivity properties of AB
- Dedrick - study impurities in H_2

Independent Analysis

- R&H and Alabama with ANL and TIAX - provide parameters for regen cost and efficiency analysis

Future Work - Hydrogen Release

▶ AB 1st fill

- Batch to continuous reactor approaches
- Cost analysis with R&H (compare with alternative methods)

▶ Enhancing H₂ purity (AB and MNH₂BH₃)

- Reduce or avoid borazine formation (preliminary results promising)
- Mechanistic studies to determine pathways to ammonia formation in metal amido boranes

▶ Solid forms

- Follow up on alternatives to fibrous materials for anti-foaming and reducing impurities
- Fuel blends (AB mixed with other H-storage materials)
- Heat/mass transfer effects in monoliths (exothermic kinetic benefit)
- Exchange information with Engineering Center



Future Work - Regeneration

- ▶ Prepare and test additional Co complexes... move toward less expensive metals, e.g., Ni, Fe ... unify process.
- ▶ Collaborate with U.S. Borax to test borate esters predicted to better match H⁻ donor abilities of Co, Fe, Ni complexes.
- ▶ Determine feasibility of recovering B-H in spent fuel.
- ▶ Collaborate with Rohm and Haas to estimate costs.
- ▶ Coordinate with LANL and UC-Davis to explore using L_nMH to regenerate R₃SnH, Si)-H nanoparticles and other candidate hydride donors.
- ▶ Analysis to determine dependence of efficiency on residual H in spent fuel, i.e., “n” in BNH_n.
- ▶ Lessons learned from AB regen to investigate regeneration of spent fuels from metal amidoboranes

Summary Table H₂ Release

compound	gravimetric	volumetric	additive	enthalpy	peak rate	temperature	NH ₃	Bz	notes
	g H ₂ /kg	g H ₂ /l		kJ/mol	g/s/kg	C	ppm	wt%	
NH ₃ BH ₃	194 (160)	146 (120)	none	-23	3.8	160	100-200	4-6	foams
NH ₃ BH ₃	"	"	none	-23	2.1	145	100-200	4-6	foams
NH ₃ BH ₃	"	"	none	-23	1.1	130	100-200	4-6	foams
NH ₃ BH ₃ + AF	155 (136)	117 (102)	Anti foaming	-23	1.1	130	??	??	no foam
AB:MCM	"	"	scaffold (1:1)	-1 (-22)	2.8	130	100-200	<1	no foam
AB:MCM	"	"	scaffold (2:1)	-10	?	130	100-200	<1	no foam
AB:MCM	"	"	scaffold (3:1)	-12	1.9	130	100-200	<1	no foam
DADB	194 (160)	??	none	-16	1.8	145	?	?	little foam
DADB	"		none	-16	0.48	130	?	?	little foam
DADB	"		none	-16	0.2	100	?	?	little foam
NH ₄ BH ₄	240	130	none	-63	?	40	?	?	little foam
LiNH ₂ BH ₃	109	52	none	?	1.76	130	200	0	no foam
LiNH ₂ BH ₃	"	"	none	?	0.44	100	2000	0	no foam
LiNH ₂ BH ₃	"	"	none	-2	0.08	90	2000	0	no foam
LiNH ₂ BH ₃	"	"	none		0.01	80	2000	0	no foam
NaNH ₂ BH ₃	76	43	none	?	0.044	80	?	0	no foam
NaMeNHBH ₃	30	??	none	?	0.043	100	?	0	no foam

Summary of rates, enthalpies and purity of hydrogen. theoretical density (measured density). Bz = borazine. ? = not yet measured, will be determined in future work. enthalpy in scaffold depends on isothermal or ramp heating



Abhi Karkamkar, Avery Luedtke, John Linehan, Wendy Shaw,
Richard Zheng, Daiwon Choi, Chris Sorensen, Tricia
Smurthwaite, David Heldebrant, Scot Rassat, Chris Aardahl,
Don Camaioni, Michael Mock, Robert Potter, Dan Dubois,
Jun Li, Jerry Birnbaum, Richard Zheng, John Linehan,
Suh-Jane Lee, Ken Rappe, David Rector, Tom Autrey

Extra Slides

- Post project transition
- Publications
- Presentations
- Response to Reviewer Comments
- Preliminary regen efficiency analysis (ANL)

Post Project Transition

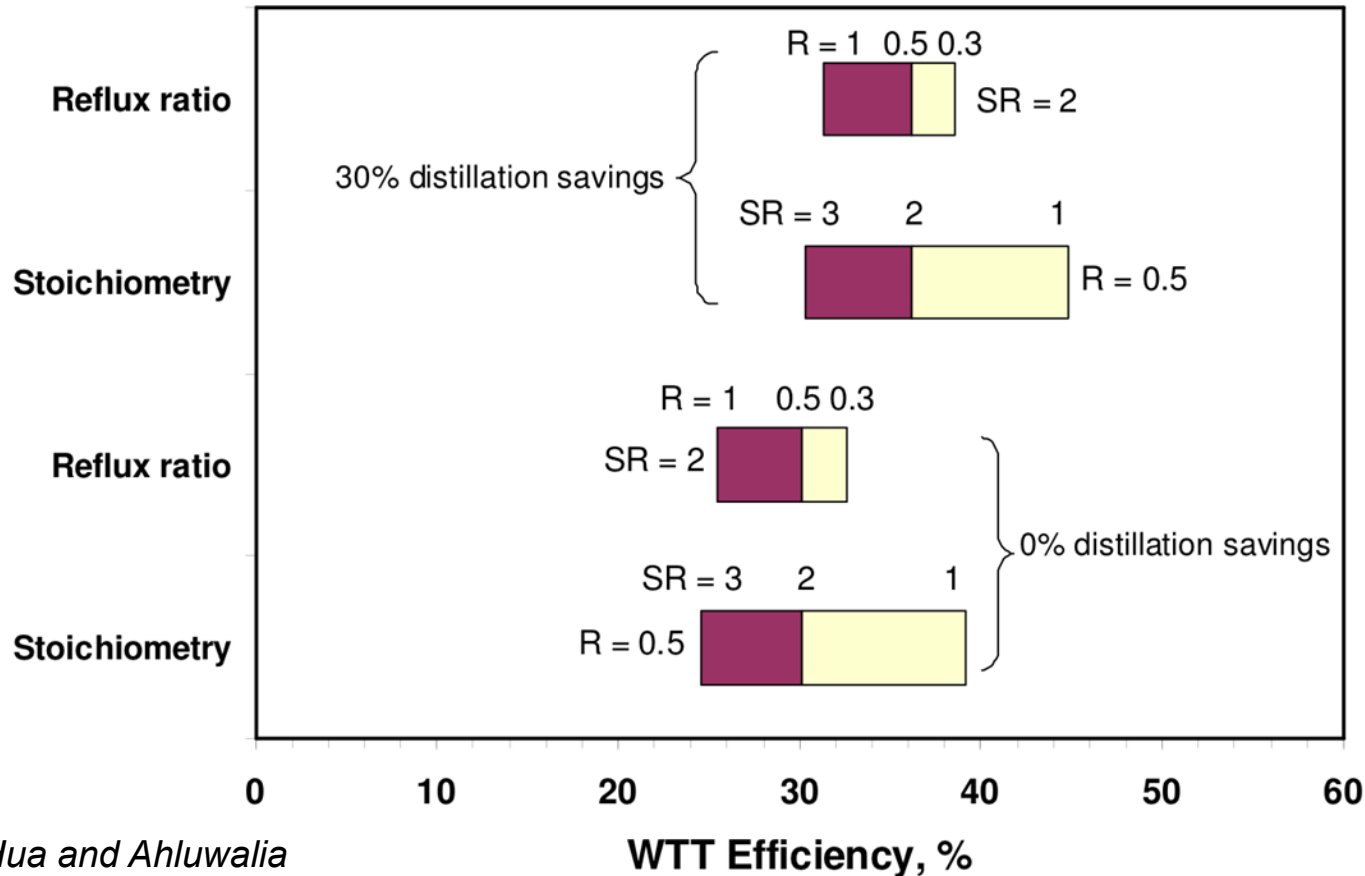
- Project due to end March 2010
- Final report will be submitted to DOE with recommendations for future research in chemical hydrogen storage materials
 - Materials
 - Regeneration schemes
- Hand off of properties information to Engineering CoE and other relevant DOE projects

ANL performed energy and efficiency analysis

- ▶ Two approaches for digesting spent fuel to $B(OPh)_3$ and NH_3 were considered.
 - Convert residual B-H to H_2 .
 - Preserve residual B-H bonds in $(BHNH)_n$.
- ▶ Preliminary estimate of well-to-tank efficiency is 25-47%.
 - Base and transition metal complex undefined.
 - Energy for separations in recycle of $B(OPh)_4^-$ not included.
- ▶ Approach that preserves residual B-H is ~10% more efficient.
- ▶ Analysis will be performed to determine dependence of efficiency on residual H in spent fuel, i.e., “n” in BNH_n .

Process efficiency sensitive to stoichiometries, separations and heat integration

FCHtool Analysis: Well-To-Tank Efficiency



Analysis for scheme that preserves B-H in spent fuel

Hua and Ahluwalia