What's the buzz on benzylamine-borane?

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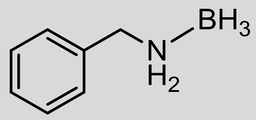
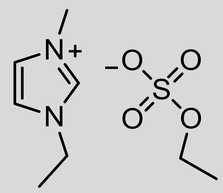
Introduction

Benzylamine-borane (BzAB)



BzAB is an N-substituted amine-borane (NSAB) that has been mixed with ammonia-borane (AB) to produce a liquid amine-borane fuel blend for use with fuel cells in vehicles. BzAB has a melting point of 57-58 ° C.
BZAB/AB mixtures are studied in both ethereal (DME, tetraglyme) and ionic liquid (IL) solvents [EMIM][$EtSO_4$])

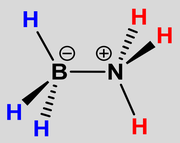


[EMIM][$EtSO_4$]

Methodology

- BzAB was synthesized at room temperature under nitrogen flow using the Schlenk line technique.
- The dehydrogenation reactions are moisture-sensitive and were thus performed in a nitrogen-filled glove box or using standard Schlenk techniques.
- The dehydrogenation products of BzAB and BzAB/AB mixtures were analyzed using NMR spectroscopy (^{11}B, ^{13}C, ^{1}H) and mass spectrometry.

Ammonia-borane (AB)

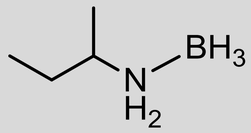


H: Hydridic B-H bonds
H: Protic N-H bonds

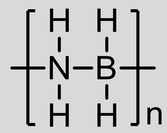
Previously in Prof. Baker's group:
Did experiments with ammonia-borane (AB) which contains 19.6 weight % hydrogen with a heterogeneous iron catalyst that can selectively dehydrogenate AB to borazine and polyborazylene at temperatures lower than 80° C.
Problem: Maintenance of a liquid fuel formulation before and after the dehydrogenation process.

Sec-butylamine-borane (SBAB)

SBAB[1] has a melting point of 2 ° C and contains 5.7 weight % hydrogen.



• Catalyzed thermolysis of SBAB/AB mixtures in ether solvent resulted in complete conversion to borazine and polyborazylene with formation of a white precipitate of poly(aminoborane), $(NH_2BH_2)_n$.



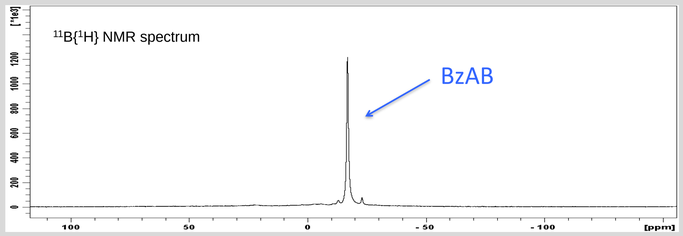
• Adding [EMIM][$EtSO_4$] reduced total hydrogen storage capacity but prevented formation of poly(aminoborane).
• AB and NSAB dehydrogenation rates have to match in order to produce 'mixed' dehydrogenation products.

1) R.T. Baker *et al. Chem.Commun.* 2011,**47,** 2922-2924.

Results

BzAB neat reaction

We started off by using BzAB in a neat reaction with the heterogeneous iron catalyst.



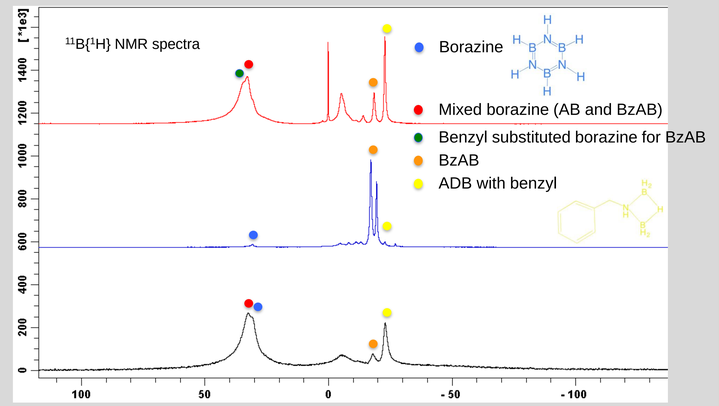
No conversion was observed.
BzAB + $FeCl_2$ in DME at 75 ° C for 5.5 hours also gave NR.

Ionic liquid

Reaction 1: BzAB + AB + $FeCl_2$ in [EMIM][$EtSO_4$] at 80° C for
4 hours
Reaction 2: BzAB + AB in [EMIM][$EtSO_4$] at 80° C for 4 hours
•Reactions with and without catalyst produced similar 'mixed' dehydrogenation products.

Mixed BzAB and AB

Next, we decided to mix AB and BzAB to increase the solubility of the products and take advantage of:
AB: lower MW of 30.9 g/mol and increased hydrogen storage content
BzAB: lower mp = 57-58 ° C and better solubility



Red spectrum = BzAB(excess)+AB+$FeCl_2$ no solvent,80° C,ON
Blue spectrum = BzAB+AB+$FeCl_2$ in DME, 75° C, 6 h (low conversion)
Black spectrum = BzAB+AB+$FeCl_2$ in tetraglyme 80° C,ON

Conclusions and future work

- Reactions of neat BzAB and BzAB/AB at 75° C have little to no conversion.
- BzAB/AB mixtures at 80° C with and without solvent result in mixed dehydrogenation products.
- Addition of iron catalyst reduced production of the linear poly(aminoborane) white precipitate.
- Dehydrocoupling can occur in the IL without the presence of a catalyst.

Future work:

- Measure the quantity of the insoluble white precipitate produced compared to that present in SBAB/AB reactions
- Focus on BzAB/AB and IL fuel blends

Acknowledgements

• University of Ottawa, Department of Chemistry
• Centre for Catalysis Research and Innovation
• Prof. Baker's group members
• Undergraduate research opportunity program (UROP) organized by Pascale Lafrance

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