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Bis(borano)hypophosphite Salts as Hydrogen Storage Media

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Hydrogen Storage for Mobile Platforms

- Metal Hydride Center of Excellence (MHCoE) is a DOE program, partnership between 8 universities, 6 national laboratories, and 3 private companies to store hydrogen for mobile applications (i.e. cars)

- MHCoE uses experimental and computational methods to investigate destabilized metal hydrides, amides and imides, alanes, complex anionic materials

New Complex Anionic Materials

- Current materials under investigation in the MHCoE include:

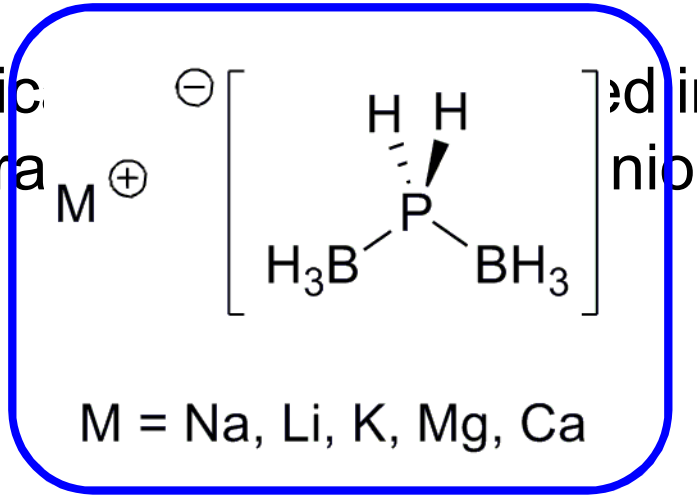
$Mg(BH_4)_2$ $Ti(BH_4)_3$

$CaB_{12}H_{12}$

$Ca(BH_4)_2 \bullet LiNH_2$ $LiNH_2 \bullet MgH_2$

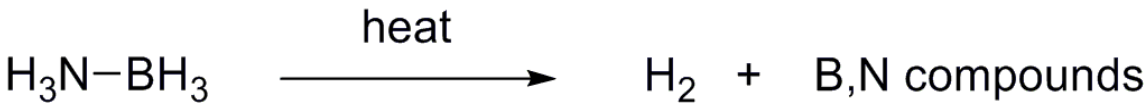
$Mg(AlH_4)_2$

- Specific ed in the salts of the bis(bora nion [PB]

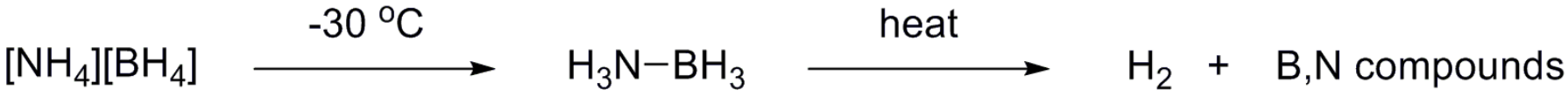


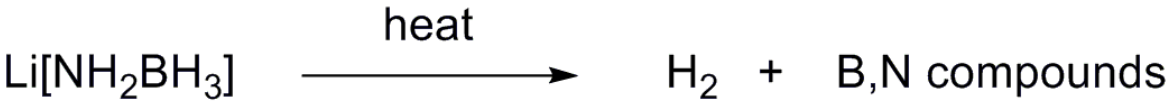
Theoretical Weight % H_2
Na[PB] = 9.7 %
Li[PB] = 12 %
K[PB] = 8.1 %
$Mg[PB]_2$ = 11 %
$Ca[PB]_2$ = 10 %

Amine-Borane and Related Compounds



- Amine-borane irreversibly releases H_2 during thermal decomposition to polymeric and cyclic B,N compounds (borazine)





- Ammonium Borohydride and $LiNH_2BH_3$ also decompose to release H_2 and form borazine and related polymers

Data collected from presentations by Aardhal and Autrey, PNNL, 2008-09.

Phosphorus-based Compounds

- Substitution of Phosphorus for Nitrogen

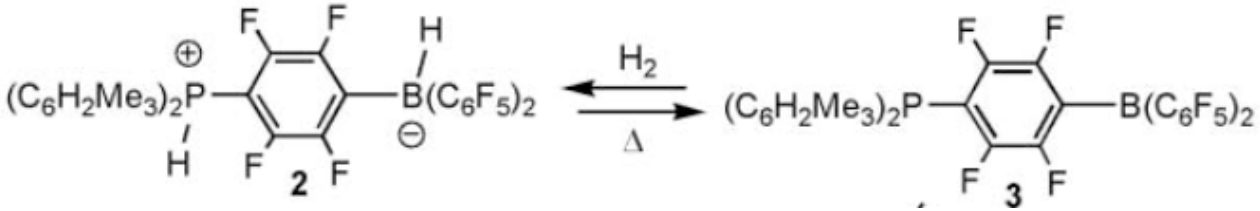
$$H_3P{-}BH_3 \xrightleftharpoons{-30\ ^oC} PH_3 + BH_3 \qquad (1)$$

$$Li[PH_2BH_3] \xrightarrow{85\ ^oC} H_2 + \text{P,B-salts} \qquad (2)$$

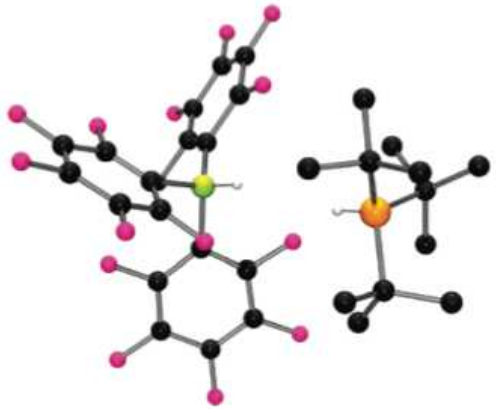
1) Gilmont, P. and coworkers, *J. Am. Chem. Soc.* 1940, *62*, 717.
2) Mayer, E. and coworkers, *Inorg. Chem.* 1971, 10, 2259.

- Reversible H_2 storage has been observed with "frustrated" B,P Lewis Acid-Base pairs

a)



b)

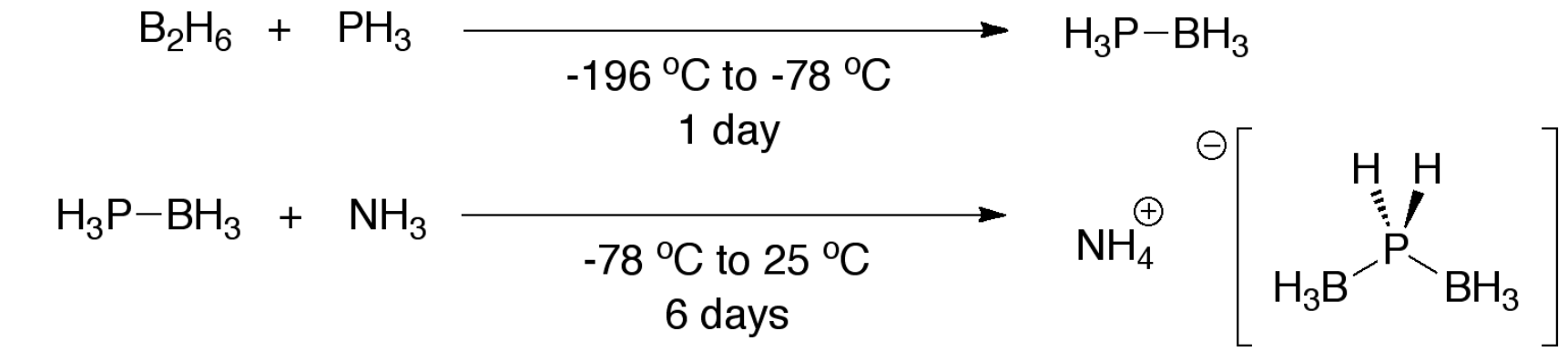


- Will hydrogen-rich B,P compounds show similar reactivity?

a) Stephan, D. W. and coworkers, *Science* 2006, *314*, 1124.
b) Stephan, D. W. and coworkers, *J. Am. Chem. Soc.* 2007, *129*, 1880.

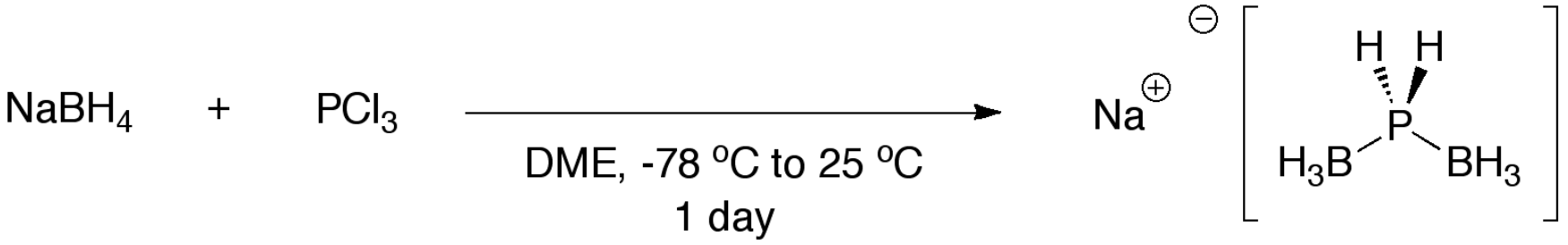
Synthesis of Bis(borano)hypophosphites

- Previous methods used PH_3, PH_3-BH_3, or PH_4I as the source of phosphorus in [PB] anion



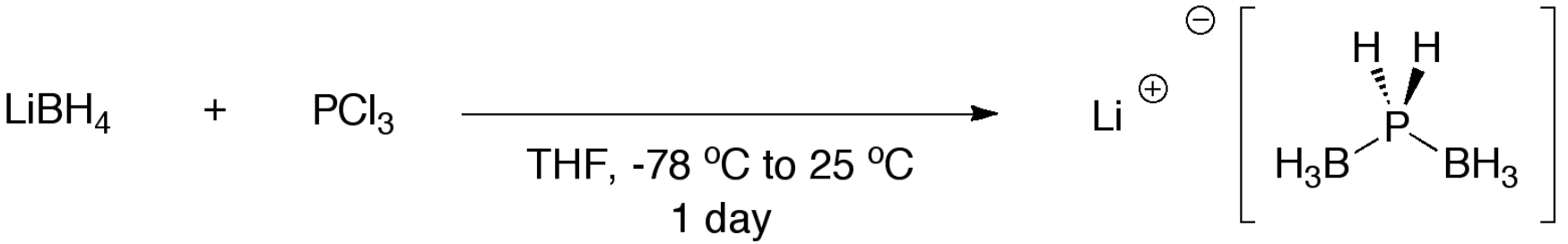
Gilmont, P. and coworkers, *J. Am. Chem. Soc.* 1940, *62*, 717.
Parry, R. W. and coworkers, Inorg. Chem. 1967, *6*, 1761.

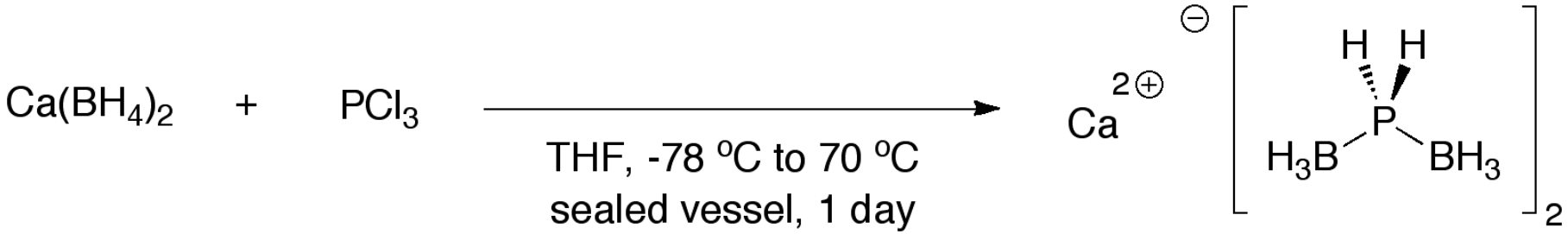
- We developed a new route in the interest of safety and convenience



Synthesis of Bis(borano)hypophosphites

- Lithium and Calcium salts made using similar methods

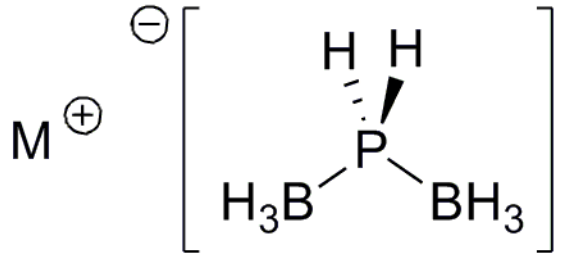




- Calcium reaction needs a sealed vessel, reaction might form PH_3 as an intermediate

Properties of Bis(borano)hypophosphites

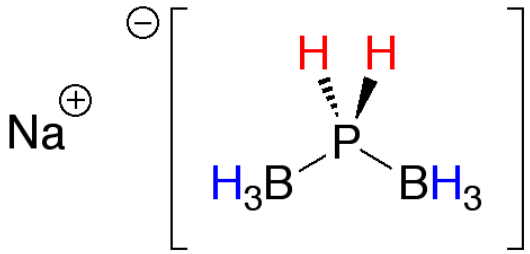
- Air and water stable
- Soluble in most organic solvents
- Forms concentrated solutions/gels
- Theoretical Weight % of H_2 is 8-12 %



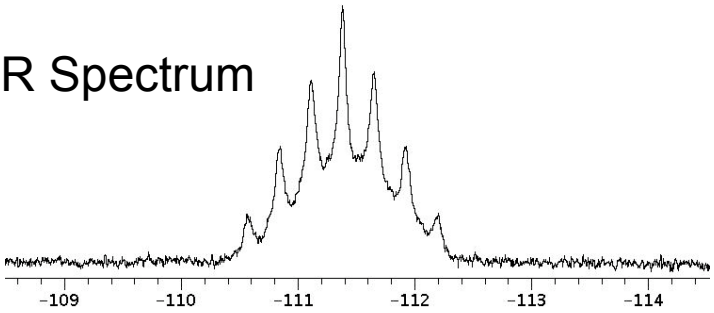
M = Na, Li, K, Mg, Ca

^{1}H and ^{31}P NMR Spectra of Na[PB]

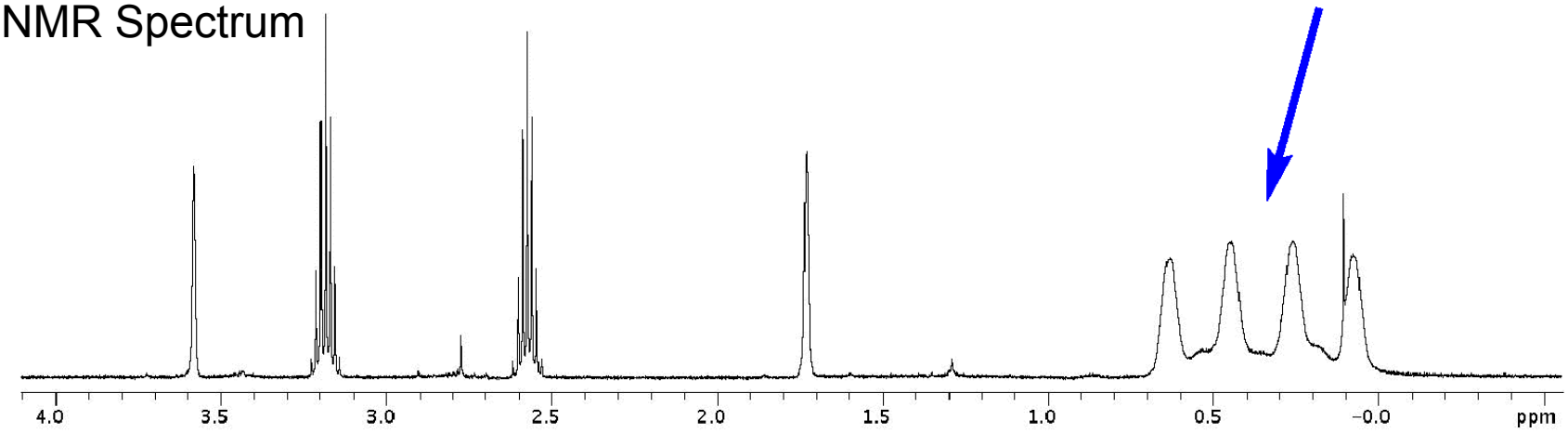
- Spectrum taken on 500 MHz Varian in THF-d_8



^{31}P NMR Spectrum

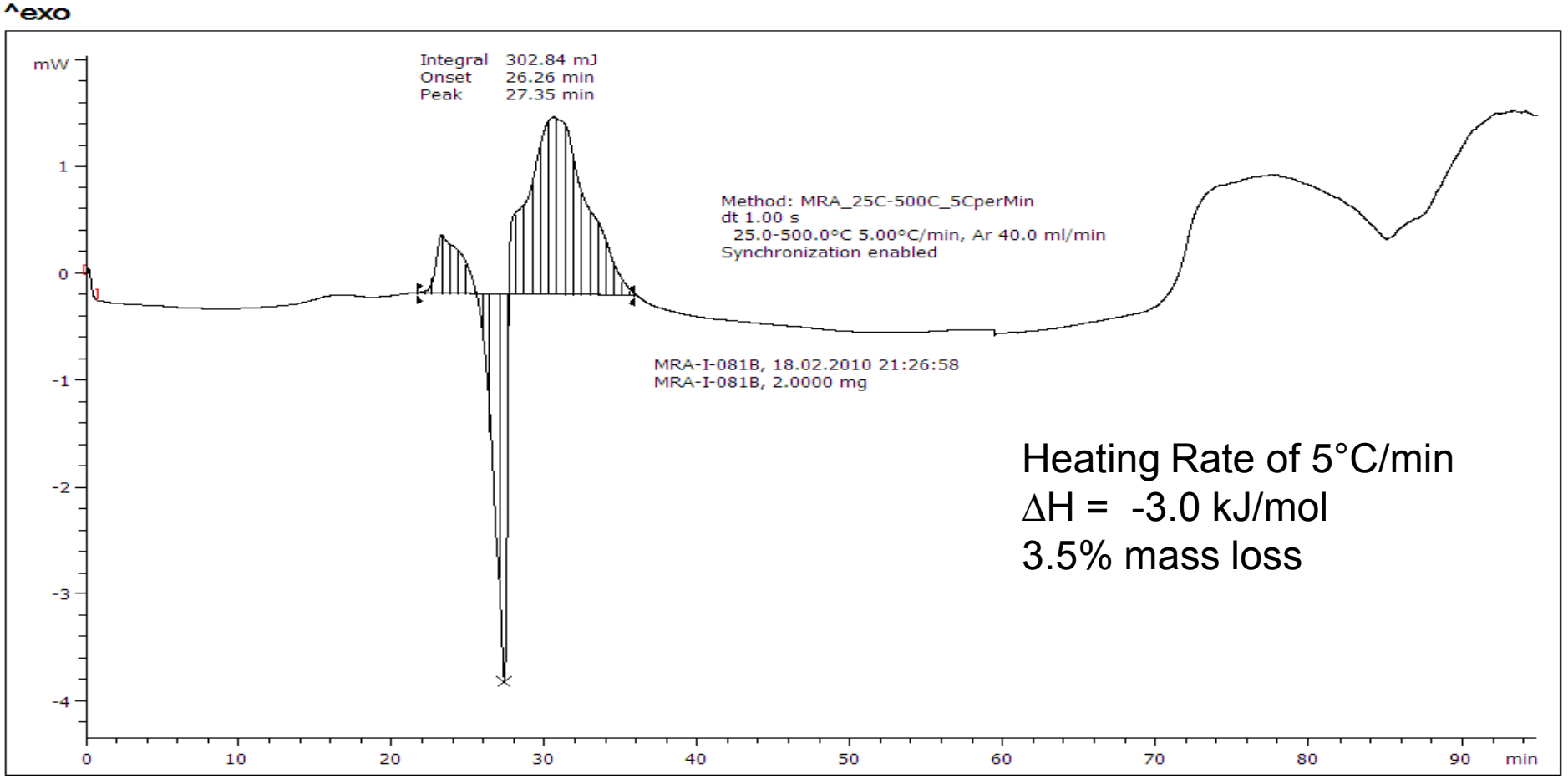


^{1}H NMR Spectrum



Na[PB] Thermal Decomposition

- Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) were performed to examine the thermal decomposition



Heating Rate of 5°C/min
ΔH = -3.0 kJ/mol
3.5% mass loss

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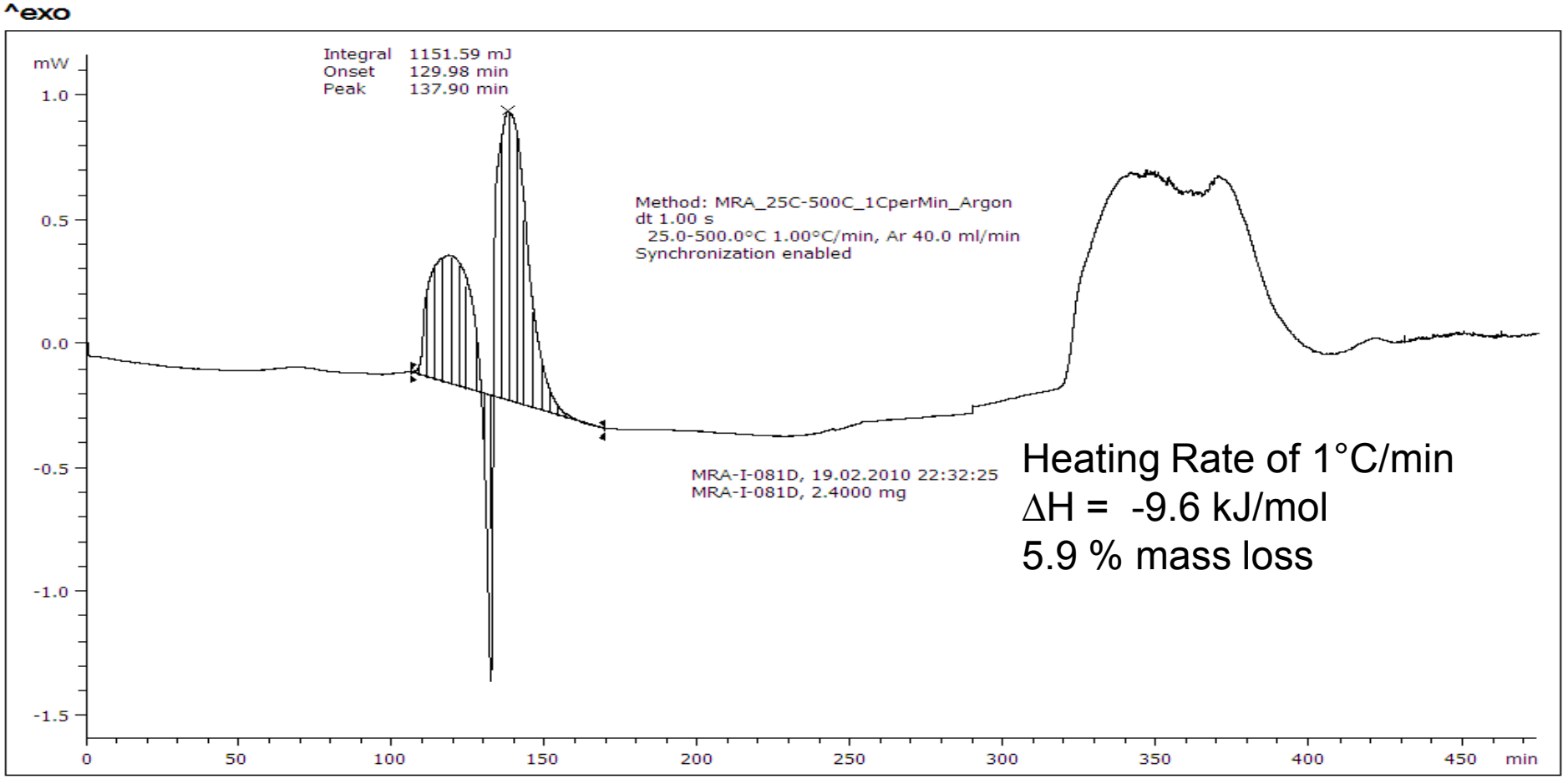

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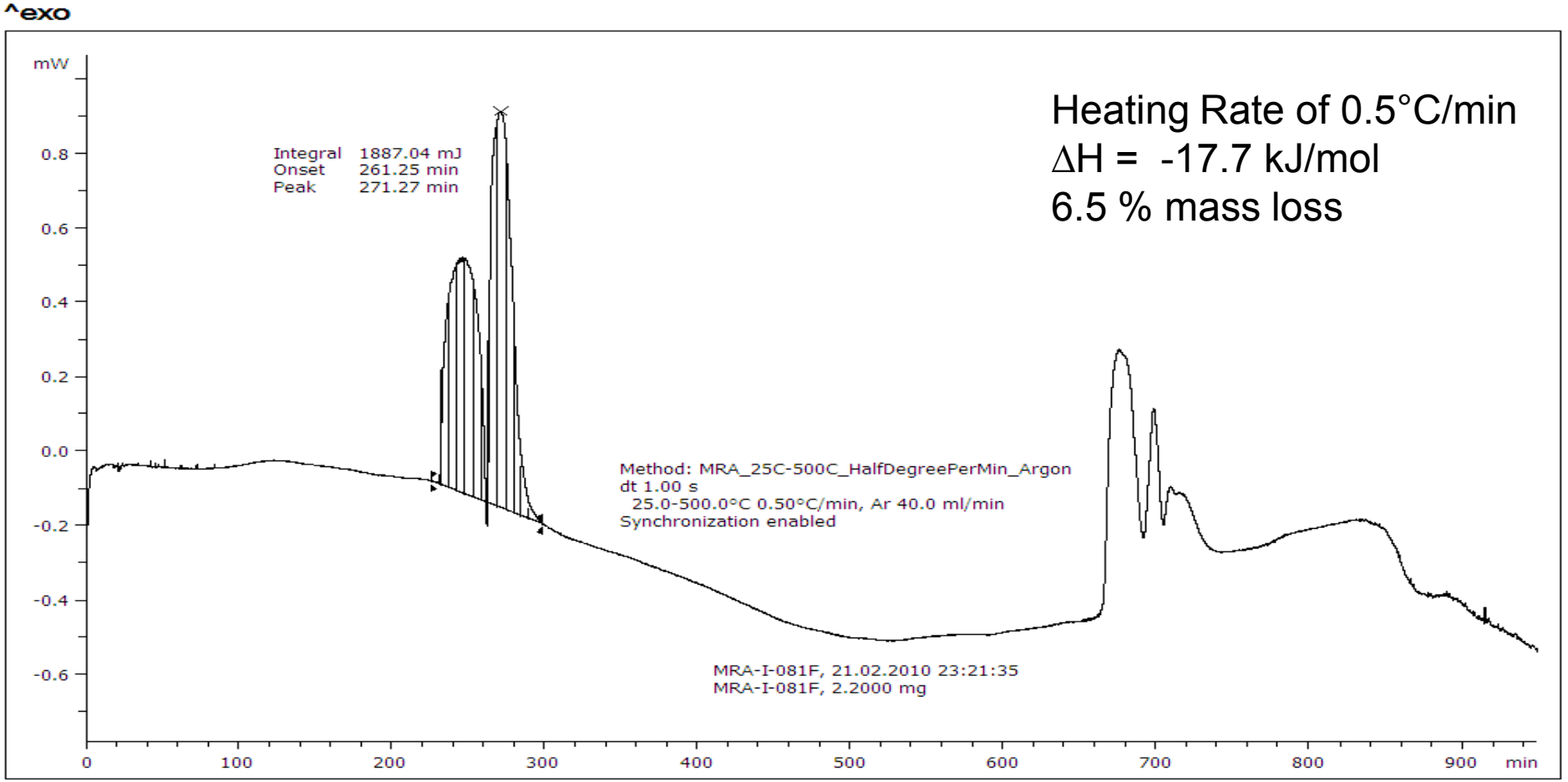
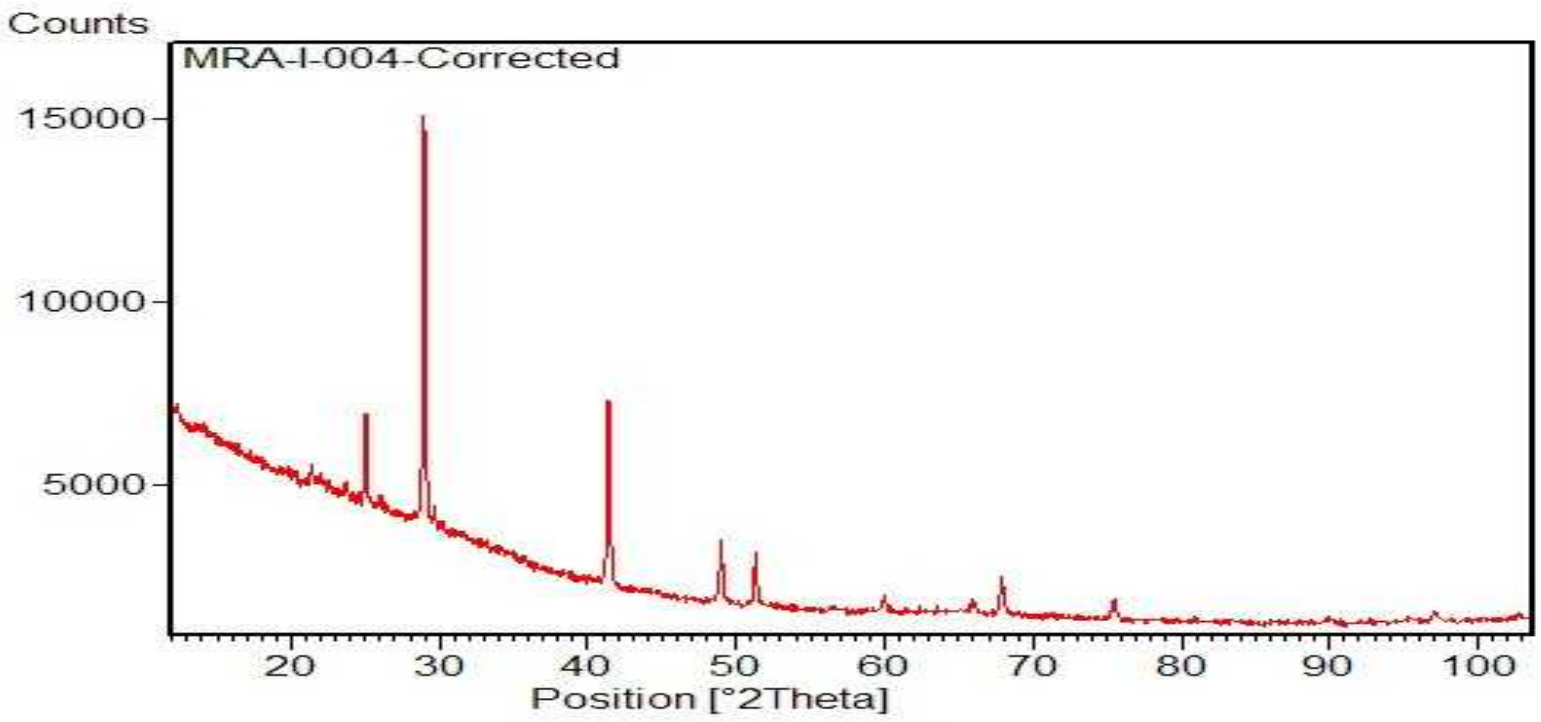


Products of Decomposition

- Samples of Na[PB] were heated to 150 °C for 18 h. This new material was deemed “spent” upon analysis by DSC and TGA (no change in mass or reactivity up to 400 °C)
- We identified the major constituent of this material as $NaBH_4$ by powder XRD



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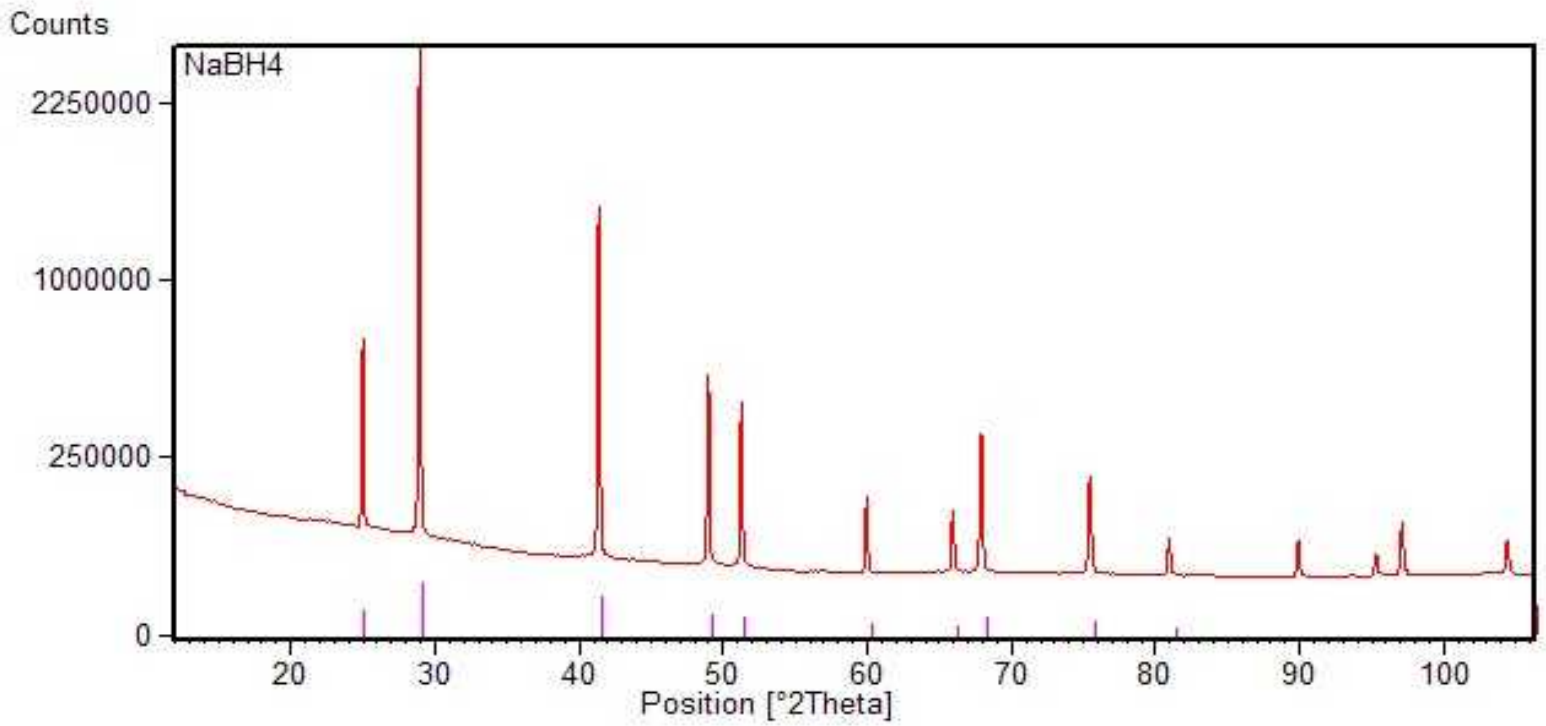
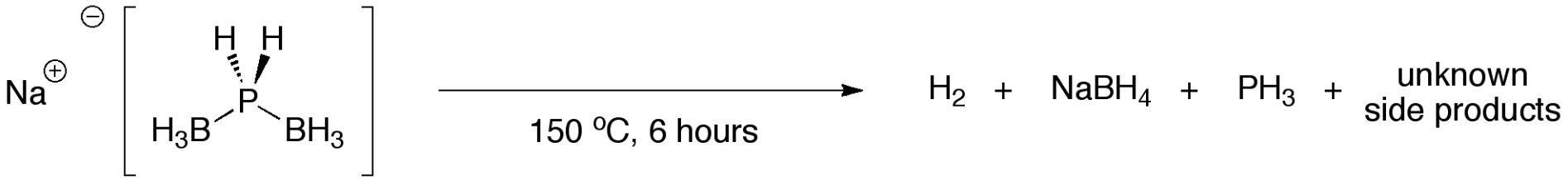
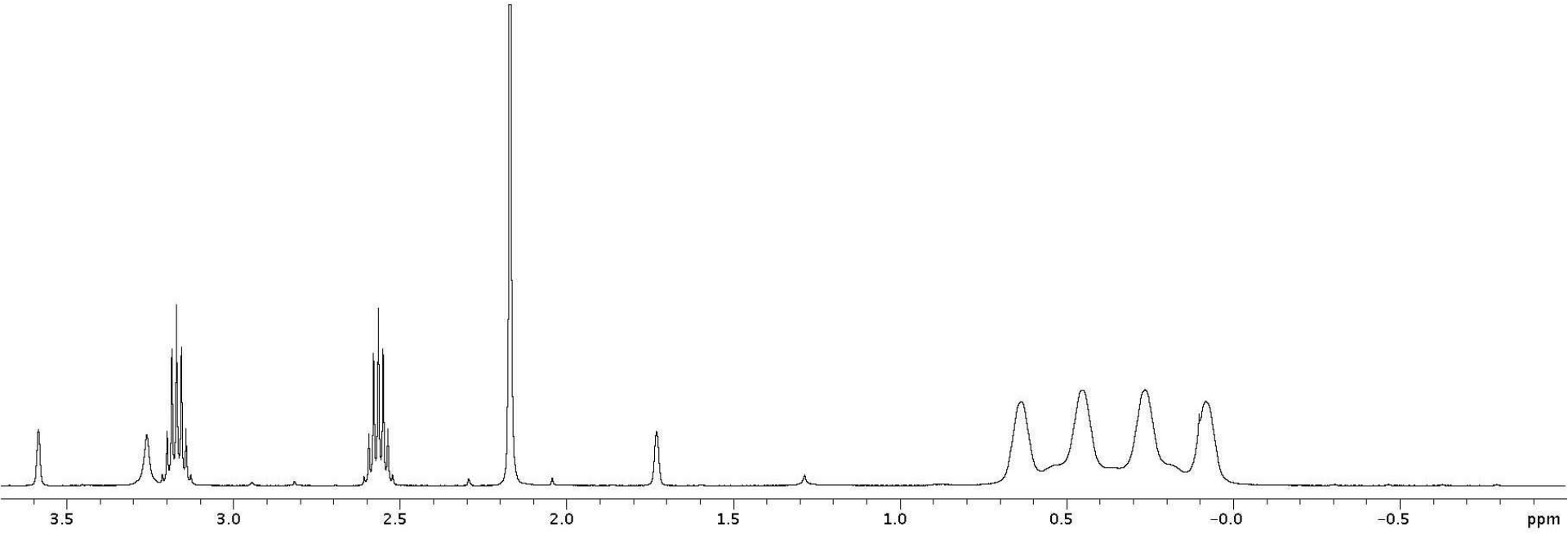


Reaction Observed by NMR

- Solution-phase thermal decomposition performed in THF-d_8





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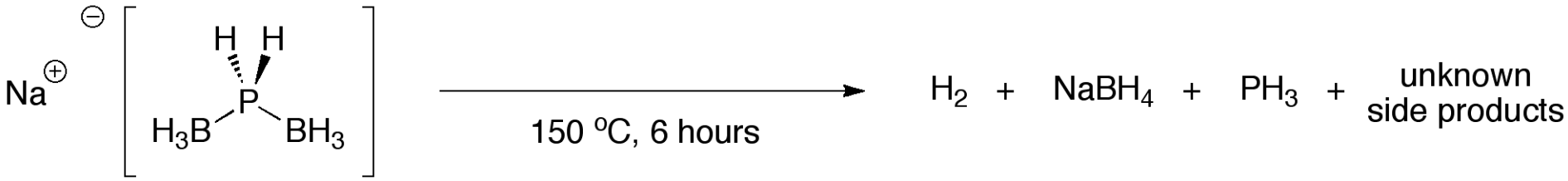

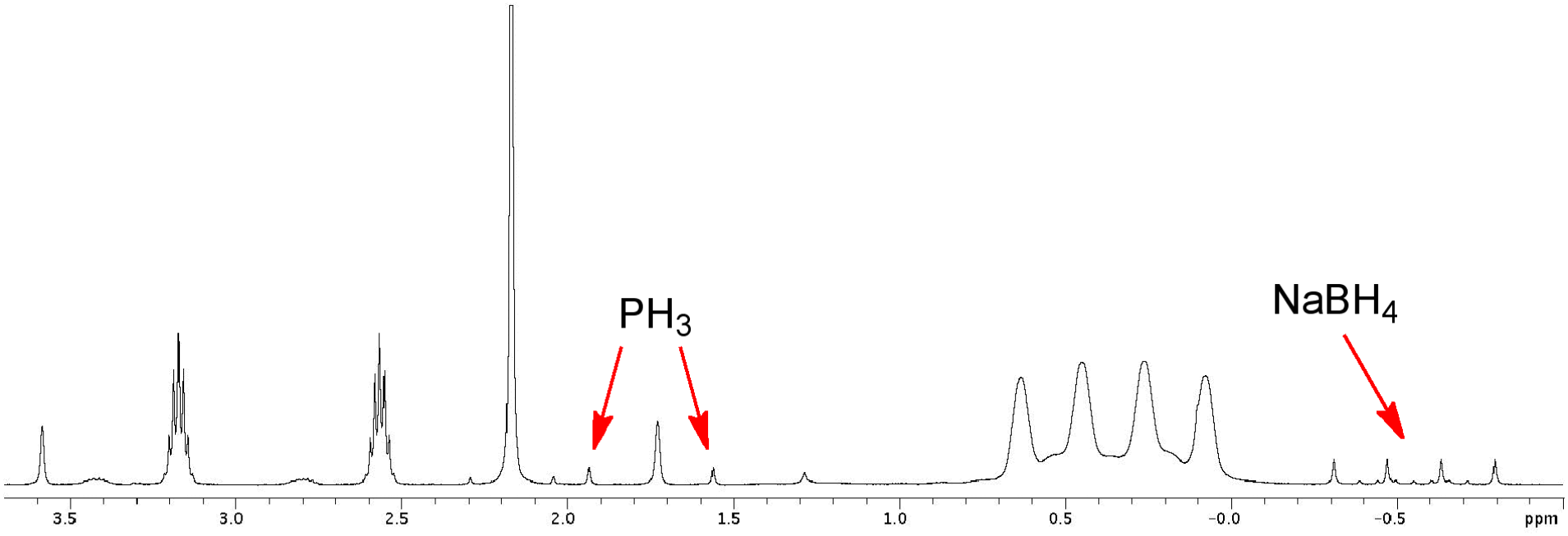

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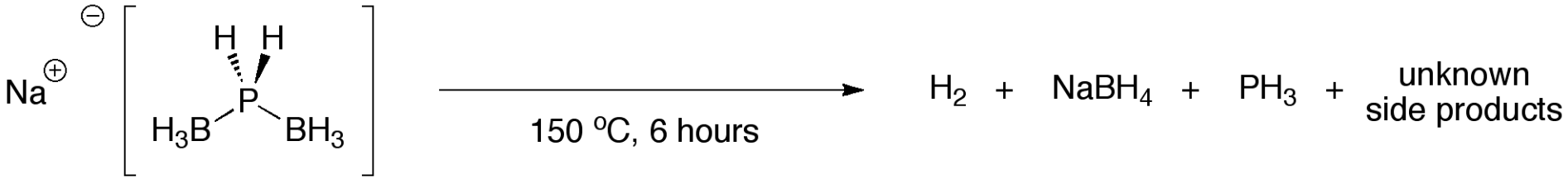
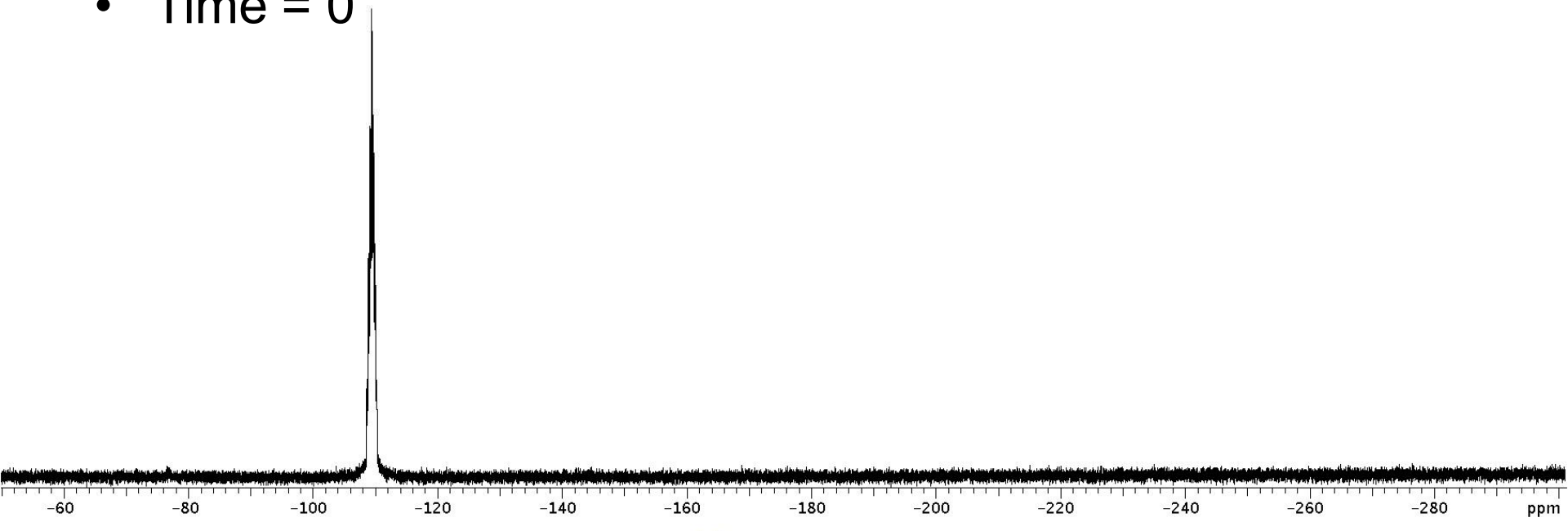


- Time = 0



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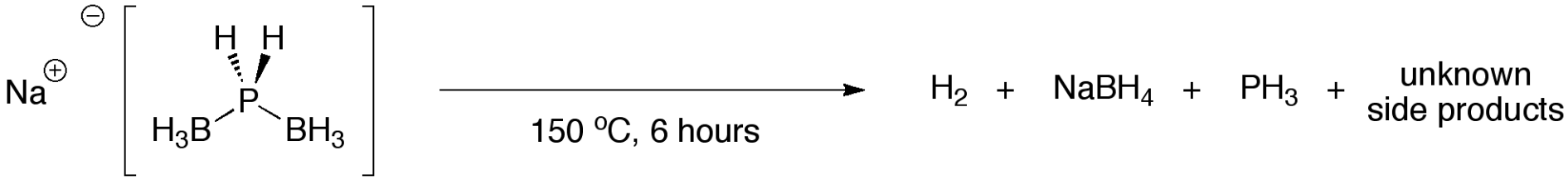
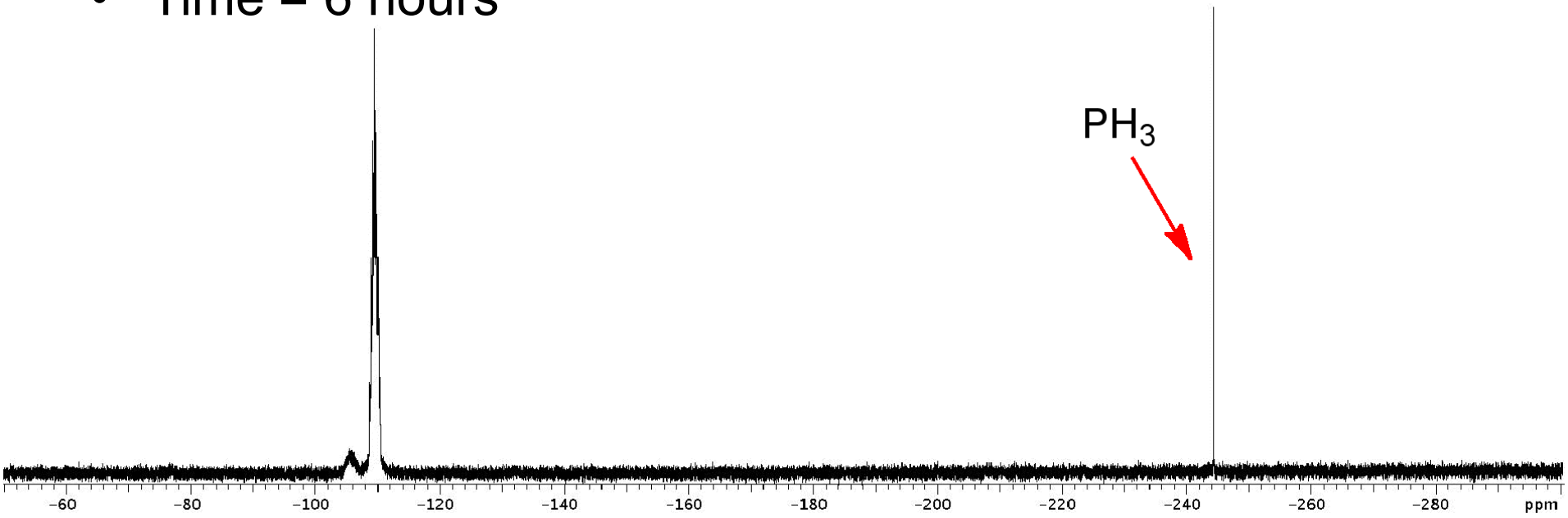
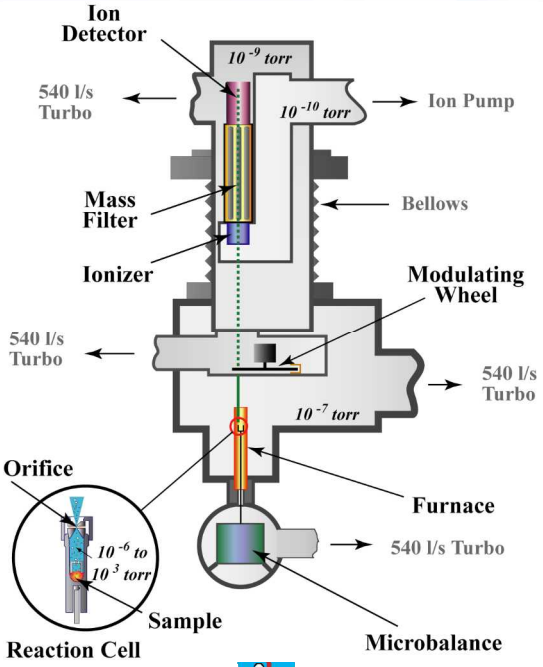


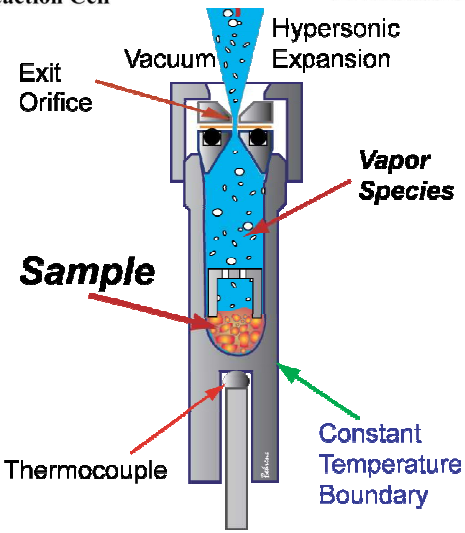
- Time = 6 hours



STMBMS

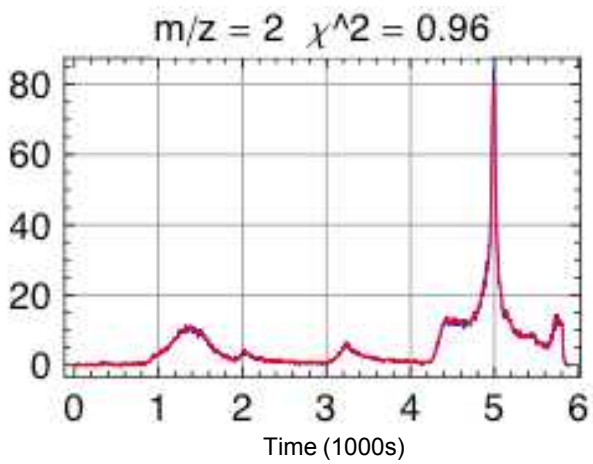
- Simultaneous Thermogravimetry Modulated Beam Mass Spectrometry (STMBMS)
- TGA coupled to a mass spectrometer
- A tool developed at Sandia to investigate energetic materials during combustion
- Can be used to obtain information regarding volatile species, sequence of species evolution, mass loss, kinetic data, partial

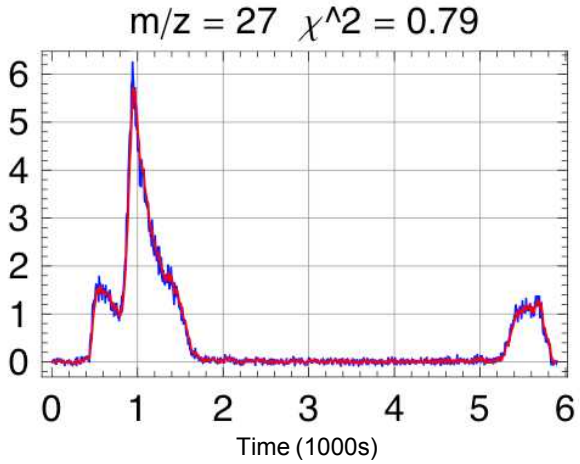


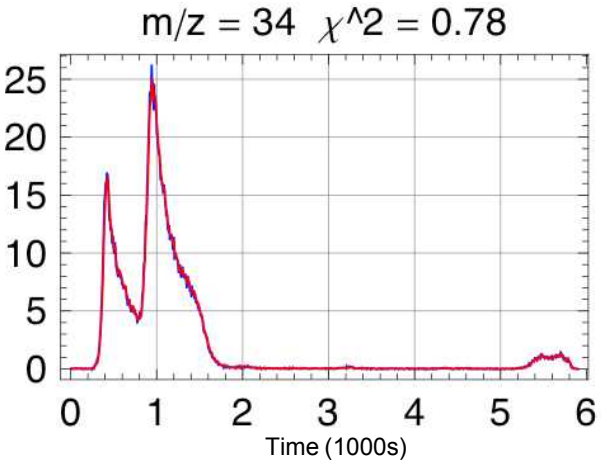


STMBMS Analysis of Na[PB]

- H_2, PH_3, and B_2H_6 have been identified as products during decomposition





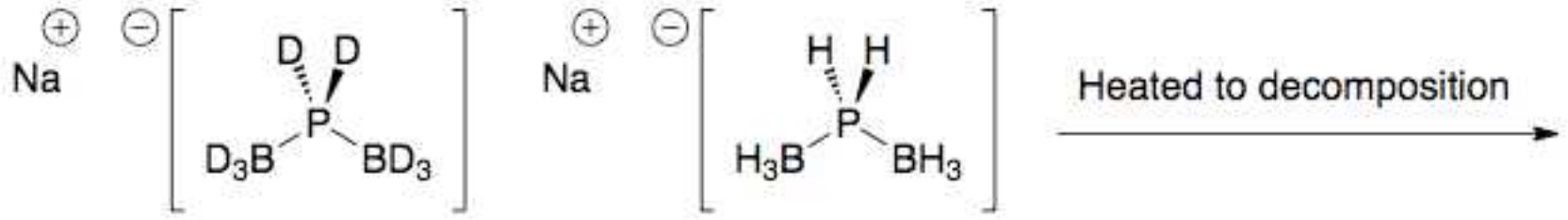


- PH_3 and B_2H_6 evolve before H_2
- Decomposition is initiating the loss of H_2?

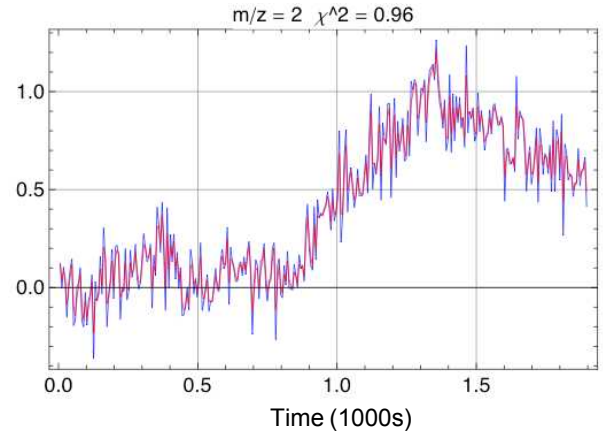
Data collected by Richard Behrens and Aaron Highley

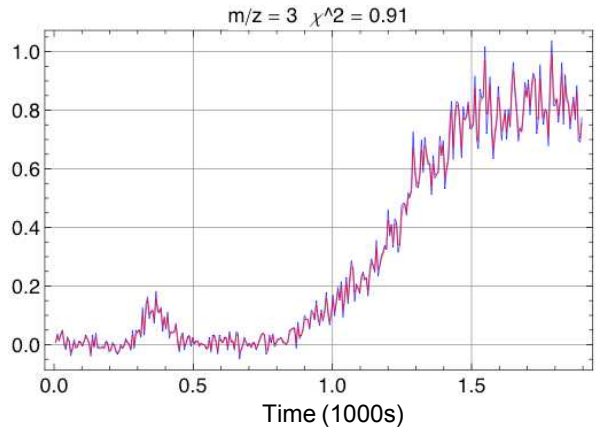
Isotopic Analysis of Decomposition

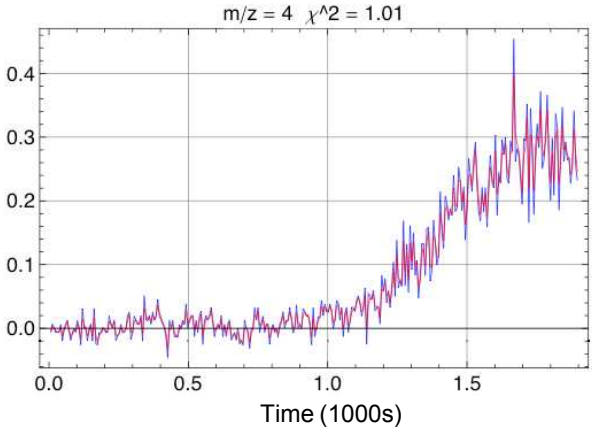
- Isotopic labeling might yield more clues about the



50/50 Mixture by moles





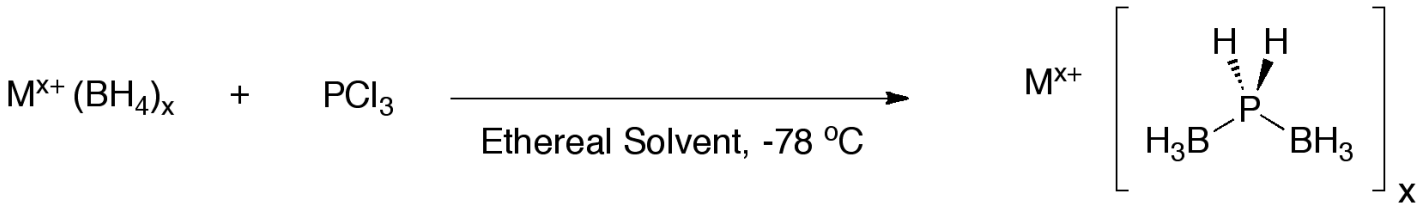


- H_2 evolves before HD and D_2, amounts are not equal to statistical distribution

Data collected by Richard Behrens and Aaron Highley

Conclusions

- Syntheses of Na[PB], Na[PB]-d_8, Li[PB], and Ca[PB]$_2$ have been developed, syntheses of other salts are still being explored



- Thermodynamic data and thermal mass loss have been measured for the Na salt

- Products of the thermal decomposition of Na[PB] have been indentified as H_2, $NaBH_4$, PH_3, and B_2H_6 using methods such as NMR, powder XRD, and STMBMS

- Hydrogenation of the “spent” material has been