INVESTIGATION OF SUBSTITUTED AMMONIA BORANES FOR CHEMICAL HYDROGEN STORAGE

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INTRODUCTION

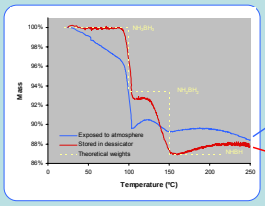
Ammonia-borane (NH_3BH_3) is a hydrogen storage material which releases 13wt% H_2 in two stages upon heating to 150ºC. The products rapidly polymerise, which makes rehydrogenation difficult. We have examined the thermal decomposition of NH_3BH_3 and two related compounds to see if they offer hydrogen storage solutions with more facile rehydrogenation paths.

$$NH_3BH_3 \xrightarrow{\sim 100^oC} NH_2BH_2 + H_2$$
$$NH_2BH_2 \xrightarrow{\sim 130^oC} NHBH + H_2$$

AMMONIA-BORANE

Thermogravimetry

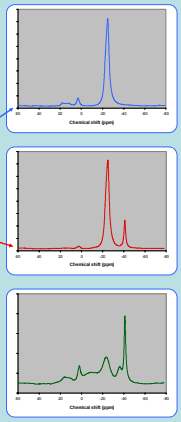
Weight change on heating at 0.5ºC/min in flowing Ar.



NH_3BH_3 is very sensitive to atmosphere, gaining 20 wt% on exposure to ambient conditions over 2 weeks.

This has a marked effect on its weight change upon heating.

Solid-state ^{11}B MAS NMR spectroscopy



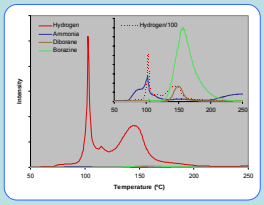
Sample exposed to atmosphere shows major resonance (-20ppm) assigned to the single boron site in NH_3BH_3. Minor resonances (0 - 20ppm) can be attributed to reaction with atmosphere.

Sample kept in desiccator with occasional vacuum treatment shows the same major NH_3BH_3 resonance and a second signal at -40ppm. The second signal matches a major resonance seen in samples which have lost hydrogen (see below).

Sample quenched after first decomposition stage shows a wide range of boron environments, consistent with an amorphous polymer.

Evolved gas analysis

Gases evolved on heating at 0.5ºC/min in flowing Ar, measured by mass spectrometer. Gases other than hydrogen are enhanced in the inset.



Hydrogen is the major gas evolved on heating.

There is a low temperature evolution of ammonia (and H_2) before the first hydrogen peak, and high temperature evolution of diborane (B_2H_6) and borazine ($B_3N_3H_6$) just after the second hydrogen peak.

METHYL AMMONIA-BORANE

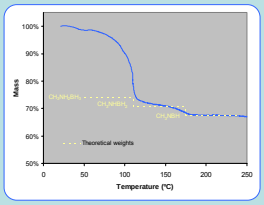
Methyl ammonia-borane ($CH_3NH_2BH_3$) is expected to decompose in an analogous manner, releasing 9wt% H_2 in two steps:

$$CH_3NH_2BH_3 \longrightarrow CH_3NHBH_2 + H_2$$
$$CH_3NHBH_2 \longrightarrow CH_3NBH + H_2$$

Unlike ammonia-borane, the products are molecular and soluble in a variety of common solvents.

Thermogravimetry

Weight change on heating at 0.5ºC/min in flowing Ar.

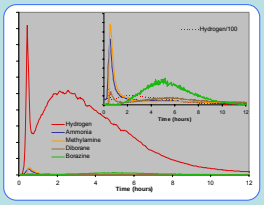


$CH_3NH_2BH_3$ exhibits severe volatility,especially around the first decomposition temperature.

The two decomposition products are comparatively stable, however, and showed little weight loss during prolonged periods at temperature.

Evolved gas analysis

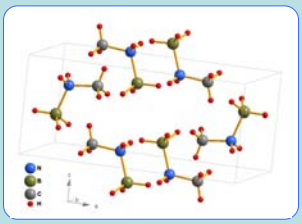
Gases evolved on heating at 80ºC in flowing Ar, measured by mass spectrometer. Gases other than hydrogen are enhanced in the inset.



Hydrogen is the major gas evolved on heating.

Ammonia and methylamine (CH_3NH_2) are also evolved during the early stages of decomposition, followed by diborane (B_2H_6) and borazine ($B_3N_3H_6$).

Crystallography



We have determined the crystal structure of $CH_3NH_2BH_3$ by single-crystal methods.

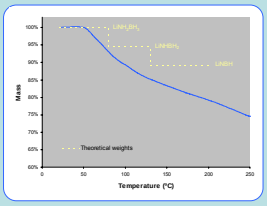
The boron and nitrogen atoms on adjacent molecules are aligned head-to-tail, giving a 2.2Å dihydrogen bond (B—H ··· H—N) often found in this type of compound.

LITHIUM AMMONIA-BORANE

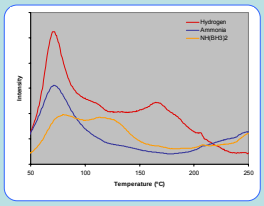
Lithium ammonia-borane ($LiNH_2BH_3$) is a little-studied compound reported in the organic chemistry literature. If it behaved in the same manner as NH_3BH_3, it would release 10.9 wt% H_2.

Thermogravimetry and evolved gas analysis

Weight change on heating at 0.5ºC/min in flowing Ar.



Gases evolved on heating at 80ºC in flowing Ar, measured by mass spectrometer.



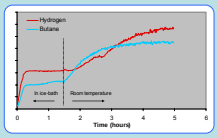
The product is amorphous and decomposes over 50°C, releasing hydrogen amongst a variety of gaseous products. The identification of $NH(BH_3)_2$ is tentative. Other mass spectrometer signals corresponding to solvents were also observed.

Synthesis

The reported synthesis generates butane from the reaction of NH_3BH_3 and butyl-lithium. However, we observed twice the volume of gas expected, and approximately equimolar amounts of butane and hydrogen during synthesis.

The product may therefore be $LiNHBH_2$.

$$NH_3BH_3 + Bu\text{-}Li \longrightarrow LiNH_2BH_3 + Bu\text{-}H$$
$$LiNH_2BH_3 \longrightarrow LiNHBH_2 + H_2$$



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