Synthesis and Characterisation of Methylammonium Borohydride.

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Methylammonium borohydride [CH3NH3][BH4] has been synthesised by the metathesis of NH4X and MBH4 in methylamine in order to determine its behaviour in comparison to ammonium borohydride [NH4][BH4]. The introduction of methyl groups is expected to disrupt the hydrogen bonding network of [NH4][BH4] and in turn alter the hydrogen release properties.

Initial room temperature X-ray diffraction studies suggest this [CH3NH3][BH4] adopts a tetragonal unit cell with lattice parameters of a = 4.9559 Å and b = 8.9203 Å. The room temperature structure shows considerable hydrogen mobility similar to that observed in NH3BH3, this hydrogen mobility has been further investigated using a combination of INS and muon spectroscopies. Neutron diffraction studies show this [CH3NH3][BH4] undergoes a phase transition at 80 K.

The kinetics and thermodynamics of these reactions have been investigated and show hydrogen release follows a similar pathway to that of [NH4][BH4]. Both compounds decompose slowly at room temperature and rapidly at ca. 40 °C to form the diammoniate of diborane or the methylated analogue [BH2(CH3NH2)2][BH4]. The first stage of decomposition has been further investigated by means on in-situ X-ray diffraction and solid state 11B NMR spectroscopy, and appears to occur in the absence of any detectable intermediates to form crystalline [BH2(CH3NH2)2][BH4]. An initial structure of [BH2(CH3NH2)2][BH4] has been proposed.

Crystal structure of [CH3NH3][BH4]  In-situ XRD of decomposition of [CH3NH3][BH4]