Electronic Supplemental Information for:

New Chemical Hydrogen Storage Materials Exploiting the Self-Sustaining Thermal Decomposition of Guanidinium Borohydride

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Experimental

General:

All solvents and reagents purchased from Sigma-Aldrich including sodium borohydride (Venpure® SF), 2-propanol (anhydrous, water < 0.003%) tetrahydrofuran (anhydrous, 250ppm BHT inhibitor) and diethyl ether (anhydrous) were used as received. Guanidinium carbonate (99%) and ethylenediamine dihydrochloride were lightly ground before using to reduce the particle size and increase the surface area. While no special precautions were taken to exclude air or protect the compounds from air during manipulations, the reactions were conducted in flasks fitted with an inlet valve connected to a slow N_2 purge and bubbler to exclude water and allow venting of any hydrogen gas formed during the reactions. Elemental analysis was preformed by Atlantic Microlab, Inc. ICP analysis for Na content was run on a TJA Solutions IRIS Advantage ICP/AE Spectrometer. ^{1}H and ^{13}C NMR were run on a Bruker Avance II 300 Spectrometer, J values are given in Hz.

Synthesis of Guanidinium Borohydride (GBH)

A mixture of guanidinium carbonate* (90.05grams, 0.50mole) and sodium borohydride (37.89grams, 1.00mole) in 200ml of 2-propanol was placed in a 500ml round bottom flask under a nitrogen blanket. The suspension was stirred for 24hr at ambient temperature (approximately 21°C) using a magnetic stir bar. Very slow gas evolution was noted and the apparent particle size of the suspended solid decreased after 24hr as the mixture became a more uniform slurry. Approximately 5 grams of Celite was added to the mixture to assist in filtering. The suspension was filtered through a 1/4inch bed of Celite filtering aid on a Buchner funnel that had been prewashed with 2-propanol. The solid was washed twice with 50ml of 2-propanol. The filtrate was combined with 300ml diethyl ether, shaken to mix thoroughly, and cooled in a -36°C freezer for 12hr. The crystalline solid product was collected on filter paper and washed 3 times with 50ml diethyl ether. After initially drying the solid under a N_2 stream (2hr at ambient temperature) the colorless crystalline compound turned to a white powder (the compound apparently crystallized as a solvate). After a final drying in vacuo (<1mmHg) overnight 54.6grams (0.729mole, 72.9% Yield) of a free-flowing white solid was obtained. m.p. 102°C (with decomposition); δ_H(300 MHz; CD_3CN) 6.40 (6H, br s, NH), -0.11 (4H, m, J_{BH} 81.4, BH) δ_C(75 MHz; CD_3CN) 159.63 (s); Anal. Calcd for $CH_{10}N_3B$: C, 16.031; H, 13.453; N, 56.086. Found: C, 16.09; H, 13.07; N, 55.81. Na content 0.125wt% (by ICP analysis).

*Guanidinium sulfate can be used in place of the carbonate without changes in the procedure with no noticeable change in the results. With guanidinium chloride very little reaction occurs and only a small amount of impure product was obtained.

Synthesis of Ethylenediamine Bisborane (EDB)

The compound was prepared following a procedure adapted from Kelly and Edwards (reference 10b). A suspension of 66.59grams (0.50mole) of ethylenediamine dihydrochloride, sodium borohydride, 37.89grams (1.00moles) and 400ml THF in a 500ml round bottom flask fitted with a stir bar was stirred for 20hr under a nitrogen blanket. The THF solvent was removed in vacuo. The resulting white solid was crushed and washed three times with 200ml of cold water to remove the NaCl product and impurities. The remaining solid crude product was collected on a medium frit and dried in vacuo for two days. Crude yield 28.30grams (0.388mole, 77.6% Yield). ^{1}H NMR in CD_3CN showed the presence of trace insoluble material and soluble impurities including BH_4^- ion. The compound was re-dissolved in THF, filtered, and after removing the solvent in vacuo, reduced to a crystalline solid that was washed twice with 50ml cold water and dried to obtain 21.45grams (0.256mole, 58.8% Yield) pure compound.
δ_H(300 MHz; CD_3CN) 4.15 (4H, br s, NH), 2.83 (4H, m, CH), 1.31 (6H, br m, J_{BH} 93); δ_C(75 MHz; CD_3CN) 47.10 (s)

Self-Sustaining Thermal Decomposition Studies

The Hydrogen yields of samples were determined by initiating SSTD reactions of pellets of known mass using a resistively heated bridge-wire sealed in a 100ml glass pressure reactor (Fisher Porter tube) that had been fitted with a gas exit valve and a Baratron pressure transducer (measuring 0-1000mm Hg) for pressure measurements. Samples were compacted into pellets of approximately 60%TMD using a plastic sleeve fitted with a Teflon plunger and lightly tapping to pack the material into a solid mass. The tube and pellet were evacuated and backfilled with pure dry nitrogen prior to initiation. The hydrogen yield was determined by measuring the volume of displaced water after collecting the ammonia impurity in a buffer solution or Dräger tube and applying P and T corrections or using PVT measurements then applying corrections for the subsequently determined ammonia impurity contribution.
Gas chromatography analysis studies were conducted using a SRI Instruments model 8610C chromatograph equipped with a PID detector and a molecular sieve column to separate hydrogen, oxygen, and nitrogen.
The ammonia impurity concentration for samples with more than 1% NH_3 were determined using a standard titrimetric method[1]. The reaction gasses were vented through an indicating boric acid buffer solution to collect ammonia prior to the volumetric measurement of the hydrogen. The buffer solution was titrated for ammonia content using standardized sulfuric acid. For samples with less than 0.1% NH_3 the concentration was measured using a predetermined volume of the reactant gas and Dräger ammonia indicating tubes according to manufacturer's specifications.

Example SSTD Reaction of GBH/EDB Pellet:

Samples of 199mg EDB and 424mg GBH were thoroughly blended with a spatula and a portion of the mixture was compacted into a 185mg, 1cm diameter pellet for testing. The pellet was placed in the bottom of the Fisher Porter Tube with a bridge wire touching the top of the sample. The system was evacuated and backfilled to ambient pressure (696mm Hg) with pure nitrogen gas and the exit valve closed to seal the vessel. The reaction was initiated by resistively heating the bridge wire using a 9V battery. Upon initiation a reaction occurred lasting about 3 seconds accompanied by the expansion of the pellet into a low density residue. The temperature of the reactor rose a few degrees and was allowed to cool before slowly venting the gas products through 25ml boric acid indicating buffer to remove the NH_3 product from the hydrogen stream. The volume of hydrogen (253ml H_2) was measured by water displacement in a leveling system providing (after applying ambient pressure and temperature correction factors) 9.53mmol H_2 or 19.25mg H_2 (10.40wt% hydrogen Yield). Titration of the indicating buffer solution to the endpoint with 0.91ml of 0.05N H_2SO_4 provides (after correcting for NH_3 remaining in the system) a total of 0.058mmol NH_3 or 0.6 mol%NH_3 in the gas stream. The pellet composition, 31.9wt% EDB and 68.1wt%GBH, was 59.2mg (0.675mmol) EDB and 125.8mg (1.68mmol) GBH. Based on each mole of reactant providing 4mole H_2 the expected H_2 yield was 9.42 mole (H_2 Yield = 101%).

1. Standard Methods for the Examination of Water and Wastewater 19th Ed 1995 Mary Ann H. Franson Managing Editor, American Public Health Association, part 4500, page 4-77.

Single Crystal Structure Report for GBH

A colorless tetragonal bipyramidal specimen of guanidinium borohydride (GBH) crystallized from isopropanol, approximate dimensions 0.18 mm x 0.20 mm x 0.31 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 296K on a Bruker SMART APEXII system equipped with a graphite monochromator and a MoKα ($\lambda = 0.71073$Å) operated at 1.5kW power (50kV, 30mA). The CCD detector was placed at a distance of 6cm from the crystal.
A total of 1464 frames were collected with a scan width of 0.5° in ω and an exposure time of 30 sec/frame. The total data collection time was 12.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a tetragonal unit cell yielded a total of 4900 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 287 were independent (average redundancy 17.073, completeness = 100.0%, R_{int} = 1.79%, R_{sig} = 0.78%) and 235 (81.88%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.7433(8) Å, b = 6.7433(8) Å, c = 24.195(3) Å, volume = 1100.2(2) Å^3, are based upon the refinement of the XYZ-centroids of 2399 reflections above 20 σ(I) with $6.272° < 2\theta < 49.87°$. Data were corrected for absorption effects using the empirical multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9816 and 0.9890.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group I4(1)/amd, with Z = 8 for the formula unit, $CH_{10}BN_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 28 variables converged at R1 = 5.45%, for the observed data and wR2 = 15.59% for all data. The goodness-of-fit was 1.180. The largest peak in the final difference electron density synthesis was 0.165 e^-/Å^3 and the largest hole was -0.174 e^-/Å^3 with an RMS deviation of 0.046 e^-/Å^3. On the basis of the final model, the calculated density was 0.905 g/cm^3 and F(000), 336 e^-.

Table 1.
Sample and crystal data for GBH.

Identification code	TG_GBH2	
Chemical formula	$CH_{10}BN_3$	
Formula weight	74.93	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.18 x 0.20 x 0.31 mm	
Crystal system	tetragonal	
Space group	I4(1)/amd	
Unit cell dimensions	a = 6.7433(8) Å	α = 90°
	b = 6.7433(8) Å	β = 90°
	c = 24.195(3) Å	γ = 90°
Volume	1100.2(2) $Å^3$	
Z	8	
Density (calculated)	0.905 Mg/cm^3	
Absorption coefficient	0.060 mm^{-1}	
F(000)	336	

Table 2.
Data collection and structure refinement for GBH.

Theta range for data collection	3.14 to 25.00°
Index ranges	-8<=h<=8, -8<=k<=8, -28<=l<=28
Reflections collected	4900
Independent reflections	287 [R(int) = 0.0179]
Coverage of independent reflections	100.0%
Absorption correction	empirical multi-scan
Max. and min. transmission	0.9890 and 0.9816
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$

Data / restraints / parameters	287 / 0 / 28	
Goodness-of-fit on F^2	1.180	
Final R indices	235 data; $I>2\sigma(I)$	R1 = 0.0545, wR2 = 0.1461
	all data	R1 = 0.0597, wR2 = 0.1559
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0906P)^2+0.1181P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0180(70)	
Largest diff. peak and hole	0.165 and -0.174 eÅ^{-3}	
R.M.S. deviation from mean	0.046 eÅ^{-3}	

Table 3.
Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for GBH.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
B1	0.5000	0.7500	0.07976(16)	0.1080(16)
N1	0.8315(2)	0.7500	0.96431(7)	0.0919(8)
N2	1.0000	0.7500	0.04534(10)	0.0883(9)
C1	1.0000	0.7500	0.99142(11)	0.0694(9)

Table 4.
Bond lengths (Å) for GBH.

B1-H5	1.07(3)	B1-H4	1.13(4)
N1-C1	1.312(2)	N1-H2	0.86
N1-H1	0.86	N2-C1	1.305(4)
N2-H3	0.80(2)	C1-N1#1	1.312(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2, y, z

Table 5.
Bond angles (°) for GBH.

H5-B1-H4	117.2(15)	C1-N1-H2	120.0
C1-N1-H1	120.0	H2-N1-H1	120.0
C1-N2-H3	114.(2)	N2-C1-N1	120.00(12)
N2-C1-N1#1	120.00(12)	N1-C1-N1#1	120.0(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2, y, z

Table 6.
Anisotropic atomic displacement parameters (Å^2) for GBH.

The anisotropic atomic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.0686(19)	0.192(5)	0.0637(18)	0.000(4)	0.000	0.000(4)
N1	0.0761(12)	0.1160(15)	0.0836(12)	0.000(2)	-0.0062(7)	0.0000(18)
N2	0.0737(18)	0.118(2)	0.0732(16)	0.000(2)	0.000	0.0000(18)
C1	0.0670(14)	0.0644(15)	0.0769(17)	0.000(2)	0.000	0.0000(18)

Table 7.
Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for GBH.

	x/a	y/b	z/c	U(eq)
H2	0.7211	0.7500	0.9821	0.11
H1	0.8315	0.7500	0.9288	0.11
H5	0.3680	0.7500	0.1041	0.166(12)
H4	0.5000	0.6560	0.0412	0.195(16)
H3	0.1090	0.7500	0.0587	0.102(8)