



**Report on Synthesis and Studies of “Generation 2”  
Lower Energy Hydrogen Chemicals**

Performed at Rowan University  
Glassboro, New Jersey

**College of Liberal Arts & Sciences**  
**Departments of Chemistry & BioChemistry**

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## **Report on synthesis and studies of “Generation 2” lower energy hydrogen chemicals**

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**Rowan University**

**Chemistry and Biochemistry**

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The primary aim of this work was to reproduce the synthesis and conduct studies of BLP generation-2 chemistry. This phase of the work is a continuation of prior work that involved studies on the lower energy state of hydrogen. During the current reporting period, sodium or potassium hydride, magnesium or calcium metal powder, titanium carbide or activated carbon support material and several halide salts were loaded in a cell and were heated to initiate the reaction. The products of the reaction, including the gases generated, were collected and analyzed. Gaseous products were analyzed using gas chromatography and mass spectrometry. The solid product was analyzed using X-ray diffraction (XRD). The reaction pathway was determined based on the starting materials and the post reaction products determined by chemical analysis. In most of the reactions the presence of magnesium hydride, the metal of metal halide reactant and an alkali halide salt were observed. A small amount of magnesium halide was also observed. However, the starting metal halide salt was absent in all the products. Liquid  $^1\text{H}$  NMR spectra after extraction with DMF- $\text{d}_7$  showed a very intense peak at approximately 1.258 ppm and at -3.84 ppm which BLP previously attributed to a lower energy hydrogen (hydrino) as molecular hydrino gas and hydrino hydride ions, respectively. The heat generated for each reaction was determined by carrying out the calorimetric studies in the Department of Engineering. For the different reaction mixtures approximately 1.6–6.5 times more energy than the maximum expected for conventional chemistry was observed. Temperature programmed desorption studies was used to rule out presence of water and/or  $\text{CO}/\text{CO}_2$  in the starting materials. In what follows, we present some of experimental studies that were carried out at Rowan.

## Background

In our prior report, we reproducibly synthesized “hydrino” trapped compounds using procedures provided by BLP. In the same study, we were able to confirm the unusual state of hydrogen, “hydrino,” using both liquid  $^1\text{H}$  NMR and MAS  $^1\text{H}$  NMR studies. For the generation of the unusual state of hydrogen, we employed a method in which alkaline halides were heated in the presence of hydrogen and a catalyst to form hydrinos. According to BLP, the alkali metal halide is capable of trapping the lower energy hydrogen as a high binding energy hydride ion [also called the hydrino hydride ion as well as molecular hydrino]. In this report, we report the results from studying BLP generation 2 chemistry. BLP has been conducting studies on generation 2 chemistry that they claim will potentially lead to a new energy source. In the generation 2 chemistry, (we witnessed at BLP and performed at Rowan University), sodium or potassium hydride, magnesium or calcium powder, a support material, and a metal halide were mixed and heated to initiate the reaction. Calorimetric studies as well as chemical characterization of the reaction products were performed using XRD, GC, MS, and TPD techniques. Liquid  $^1\text{H}$  NMR was also carried out on some of the samples. We report here the results of these reactions carried out at Rowan using chemicals procured by us, and using both 0.05 mole (5X) and 0.5 mole (50X) scale reactors. We initially assessed possible chemical reactions occurring and their energies. The enthalpies of the most energetic reactions possible were compared with the actual heat measured calorimetrically in the smaller 5X reactors and larger 50X reactors.

## Chemicals and Procedures

Titanium carbide, TiC, tin iodide,  $\text{SnI}_2$  (99%), iron bromide,  $\text{FeBr}_2$  (98+%), magnesium metal powder, Mg (99.8%), potassium hydride, KH (30-35% wt% in mineral oil), indium chloride,  $\text{InCl}$  (99.995%), cobalt iodide,  $\text{CoI}_2$  (99.5%), europium bromide,  $\text{EuBr}_2$  (99.99%), manganese iodide,  $\text{MnI}_2$  (98%), calcium, Ca (98.8%), and silver chloride,  $\text{AgCl}$  (99.9%) were all supplied by Alfa Aesar. The anhydrous hexane ( $\geq 99\%$ ) was supplied by Sigma Aldrich and sulfur hexafluoride,  $\text{SF}_6$  (99.9%) was from GTS-Welco. In preparation for the first reaction, titanium carbide was first dried in a flask under a vacuum of approximately 50 mTorr at 200 °C for 14 hours and then transferred to the glove box. The potassium hydride was washed inside the glove box with anhydrous hexane four times after decanting the mineral oil. The KH was further dried in the anti-chamber of the glove box for 4 hours to remove residual hexane and other organic residues, and later transferred into a

sealed container within the glove box. As will be described later, temperature programmed desorption (TPD) studies were done on the starting materials, manganese iodide, titanium carbide and other salts to quantify any condensable gas(es) such as water and/or CO<sub>2</sub>/CO present.

For a 50X reaction, 83.0 grams of KH, 50.0 grams of Mg, 200.0 grams of TiC and 154.0 grams of MnI<sub>2</sub> were weighed and thoroughly mixed in a large beaker inside the glove box. A 2 liter cell was transferred to a glove box and the reaction mixture was quantitatively transferred into the cell and then the cell closed. The loaded cell was taken to the Technology Park in Rowan University where calorimetric studies were carried out. For a 5X reactor, 8.30 grams of KH, 5.0 grams of Mg, 20.0 grams of TiC and 15.40 grams of MnI<sub>2</sub> were used. The reaction was repeated with MnI<sub>2</sub> replaced by FeBr<sub>2</sub>, SnI<sub>2</sub>, InCl, CoI<sub>2</sub>, EuBr<sub>2</sub>, AgCl and SF<sub>6</sub>.

For the solution <sup>1</sup>H NMR measurements, a post reaction sample from NaH +MgH<sub>2</sub> + activated carbon and 0.03 moles of SF<sub>6</sub> gas was extracted using DMF-d<sub>7</sub> solvent in a glove box. The clear liquid, just above the solid material, was transferred to an NMR tube and tightly capped. <sup>1</sup>H NMR was recorded using a 400 MHz Varian Oxford AS400 NMR system. All chemical shifts in <sup>1</sup>H NMR spectra were relative to TMS.

### **Temperature programmed desorption (TPD) studies**

The desorption behavior of materials was studied using a Chembet 3000 chemisorption unit of Quantchrome Corporation with a thermal conductivity detector (TCD). The initial task of this phase of analysis was to quantify water present, if any, in starting materials. Argon was used as a carrier gas, and dry ice was used for the separation of water (by condensation) during the course of desorption experiments. Approximately 0.1 grams of the sample was loaded into the TPD cell under argon environment. The cell was then placed in a thermal heater and connected to a gas line (including stainless steel tubing and reservoir). Any condensed water would be carried into the TCD analyzer when the dry ice dewar was removed and the trap was thawed to room temperature. Appendix A shows the TPD traces of the starting materials (TiC and MnI<sub>2</sub>) suggesting a negligible amount of water and CO<sub>2</sub> present in the materials.

An independent TPD analysis was also performed using the ideal gas law. Approximately 0.1 grams of the starting chemical sample was loaded into a TPD cell under argon, the cell was then placed in a thermal heater and connected to a gas line (including stainless steel tubing and reservoir). Before heating, the sample and gas line were evacuated to ~10<sup>-5</sup> Torr of pressure. The cell was then heated

slowly to  $\sim 500$  °C in order to desorb all of the water present in the sample. The evolved gas was expanded into a reservoir of known volume. The gas line was then submerged into a liquid nitrogen dewar in order to condense any water vapor or other gas(es) present from the thermal desorption. After evacuating the noncondensable gases, the cold trap was removed to allow the reservoir to reach room temperature and evaporate any condensed gas with temperature increases. In the experiment, cell temperature, room temperature, and gas pressure were monitored and recorded by a Labview program.

The quantity of gas obtained could be calculated using the ideal gas law (Equation 1) using the measured pressure, temperature and volume.

$$PV = nRT \quad (1)$$

The results of the TPD of the TiC and MnI<sub>2</sub> starting materials are given in Appendix A. Since liquid nitrogen was used as the cold trap, any gas with a boiling point above  $-196$  °C would have been condensed. As shown, the total condensable gas was negligible; thus, the material contained minute quantities of H<sub>2</sub>O (and/or CO<sub>2</sub> and CO) from both TiC and MnI<sub>2</sub>. Their contribution to the heat energy of the reaction was considered to be small enough to be neglected in the heat balance calculations.

### **Analysis of reaction products**

Before collecting the gas for MS and GC analysis, the pressure and volume of the gas in reactor was measured by connecting the reactor to a pre-evacuated reservoir (known volume) with a pressure gauge. Using the known combined volume, measured pressure and temperature, the moles of gas were determined using the ideal gas law. The gas from the reaction was then transferred to an empty cell for mass spectroscopic identification and quantitative gas chromatography. Gas chromatography (GC) showed that most of the gas generated during the reaction was methane. Figure 1 shows the gas chromatogram of the gases generated during the reaction. Argon is already present as all the chemical manipulations are carried out in this atmosphere. The gas was loaded into a six-port rotary valve from gas container with a gas line before the injection. Prior to the gas sample loading, the sample loop ( $\sim 3$  ml) in the six-port rotary valve was sufficiently evacuated ( $\sim 10^{-5}$  torr) to remove any residual gas/contaminant. The oven temperature was set at  $80$  °C, the injector was set to  $100$  °C, and the detector was set to  $120$  °C. Helium was the carrier gas and a flow rate of  $43.4$  ml/min was employed. Calibrations using pure gases H<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub> were

performed prior to testing. Figure 2 shows the mass spectrum of the gases generated during the reaction. To quantify the amount of methane found in the gaseous phase, a calibration curve of methane gas was obtained (Appendix A). In the case of the reaction mixture 83g KH +50g Mg + 200g TiC + 154g MnI<sub>2</sub> a quantitative analysis of the gaseous phase indicated that 16.0% volume of the gas produced was methane. Since the total gas pressure was about 1 atm, and the volume of methane was 384 ml (2400 ml × 16%), the moles of methane in the product was 0.01575 mole (room temperature 24 °C).

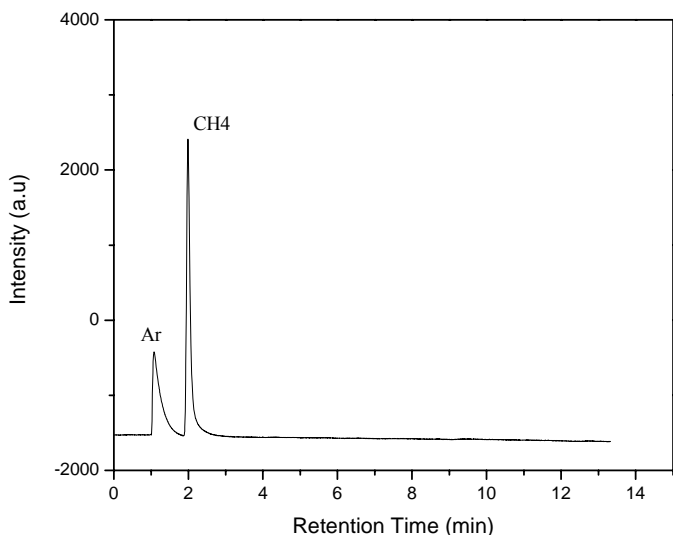


Figure 1. Gas chromatograph of contents of gas phase following the reaction.

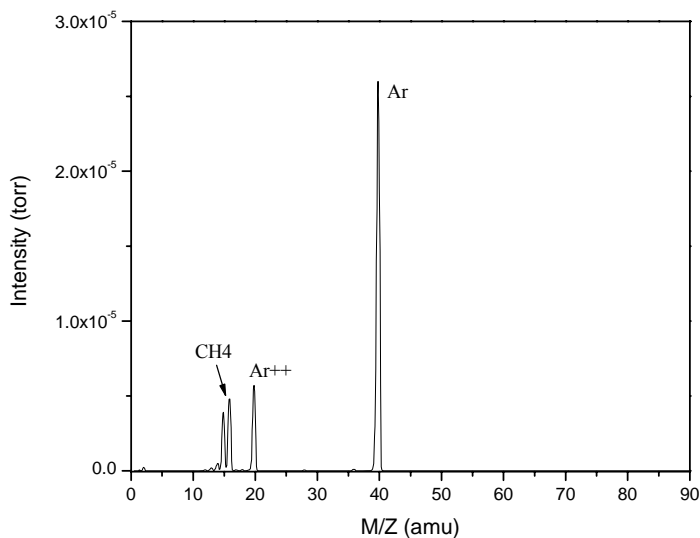


Figure 2. MS spectra of gas following the reaction. Methane is the minor component while Ar was the predominant component as the cell was loaded under argon in dry box.

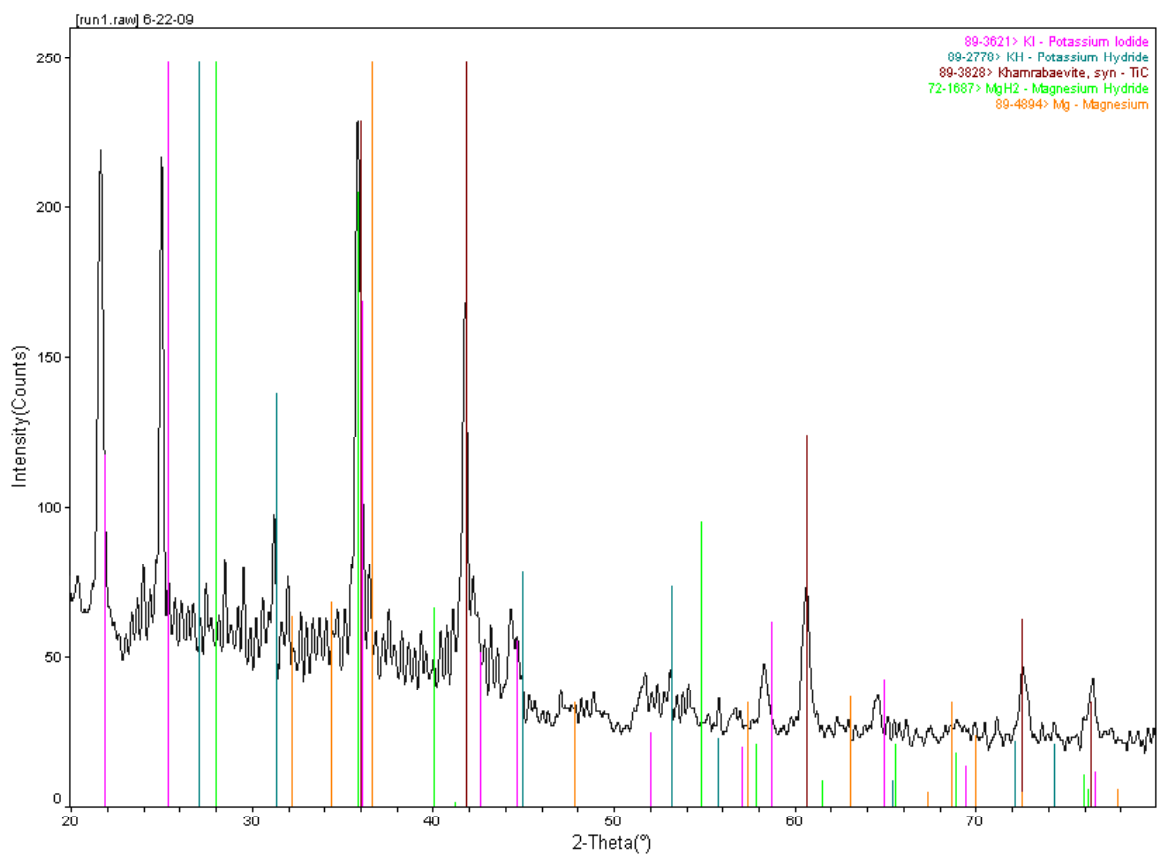
## X-ray diffraction (XRD)

In this part of the work, we have carried out several slow scans of post run products from the Technology Park in Rowan University. The samples were loaded in hermetically sealed sample holders (Bruker Model #A100B37) in a glove box under argon and wax sealed. Diffraction patterns were recorded using Scintag X2 Advanced Diffraction System with an operating voltage set to 40 kV and current of 30 mA. Patterns were recorded in a step mode [0.02 Deg/min] in the  $2\theta$  range 10-70 using a residence time of 8 seconds. The diffraction patterns of post reaction mixture of manganese iodide, potassium hydride, magnesium and titanium carbide recorded at Rowan are shown in Figure 3. The diffraction patterns from a library were matched to the diffraction pattern obtained from the post run samples. From the diffraction patterns potassium iodide, magnesium metal, manganese metal, titanium carbide, and magnesium hydride were observed. The diffraction patterns obtained at Rowan and at a commercial laboratory were similar.

Figure 4 shows the diffraction patterns obtained from the commercial laboratory. Quantitative XRD analysis from a commercial laboratory shows KH ( $2.6 \pm 0.3 \%$ ), Mg ( $4.3 \pm 0.4\%$ ), Mn ( $3.7 \pm 0.4\%$ ), KI ( $22.7 \pm 0.3\%$ ),  $\text{KMgH}_2$  ( $5.7 + 0.2\%$ ) and TiC ( $61.0 \pm 0.8$ ). Manganese iodide was absent from the reaction products suggesting that it may be the limiting reactant. This was the case based on the mole ratios of the reagents of the reaction mixture. Accordingly, all the energy calculations were based on the actual amount of  $\text{MnI}_2$ .

Figure 5 shows the XRD Diffraction patterns of post-reaction sample phase identification at Rowan. Reactants included potassium hydride, magnesium, titanium carbide and indium chloride. From the diffraction patterns we observe that there is no indium chloride in the post reaction mixture, indicating that it was consumed. The post reaction sample contains magnesium, traces of magnesium hydride, and magnesium chloride, and indium metal. There were other smaller peaks that could not be assigned and the phase identification is not conclusive.

XRD of post reaction mixtures containing (i) KH+Mg+ $\text{SnI}_2$ +TiC (ii) NaH+  $\text{MgH}_2$ +  $\text{SF}_6$  +activated carbon, and (iii) KH+Mg+AgCl+activated carbon are given in the appendix section E. Although we were not able to establish the completion of the reaction, we however observe some magnesium hydride, in all cases. The XRD also suggests that all the initial halide salt used in the starting mixture was absent in the post reaction mixture.



aterials Data, Inc.

[XRD]chemist|c:\Program Files\Scintag, Inc\datafiles\BLP> Wednesday, Jul 01, 2009 09:32a (MDI/JADE6)

Figure 3. XRD Diffraction patterns of post-reaction sample phase identification at Rowan. Initial reactants included magnesium, manganese iodide, titanium carbide and potassium hydride.

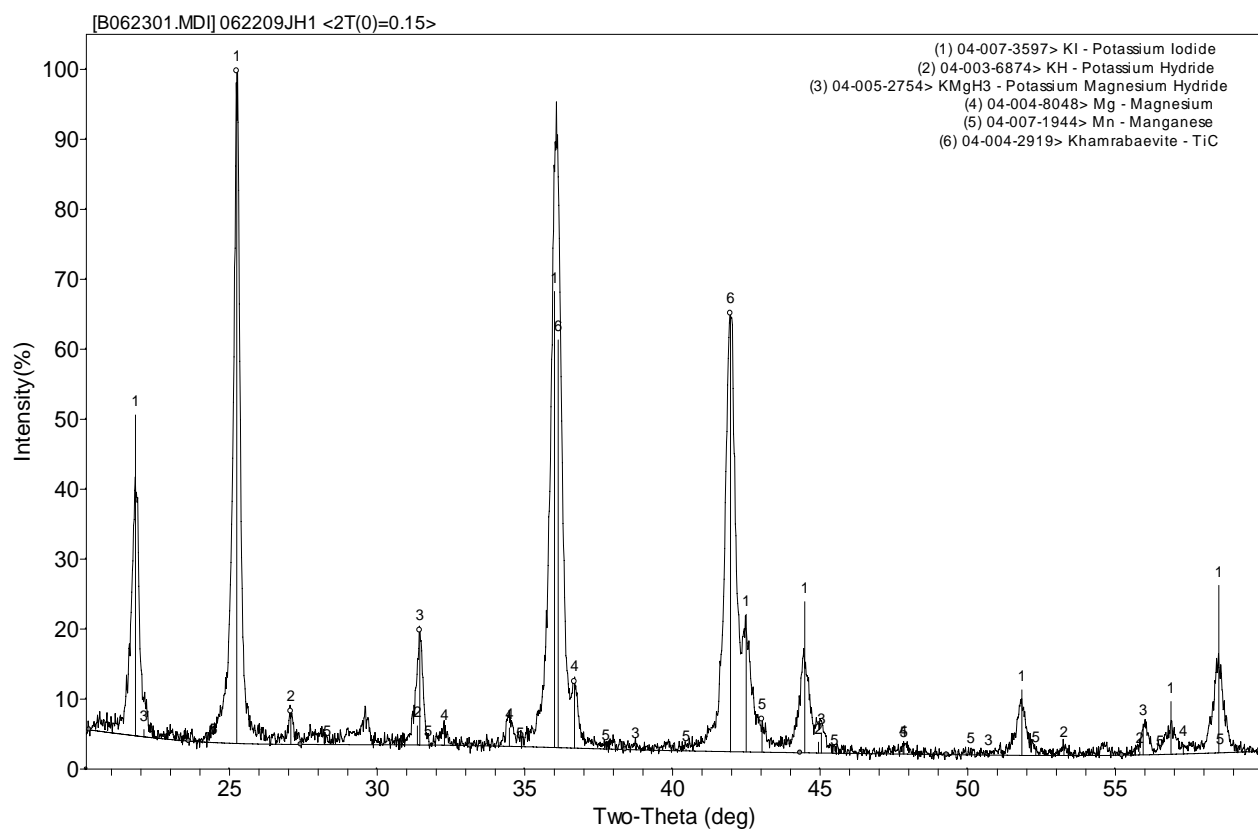


Figure 4. XRD Diffraction patterns of post-reaction sample phase identification at a commercial laboratory. Initial reactants included magnesium, manganese iodide, titanium carbide and potassium hydride.

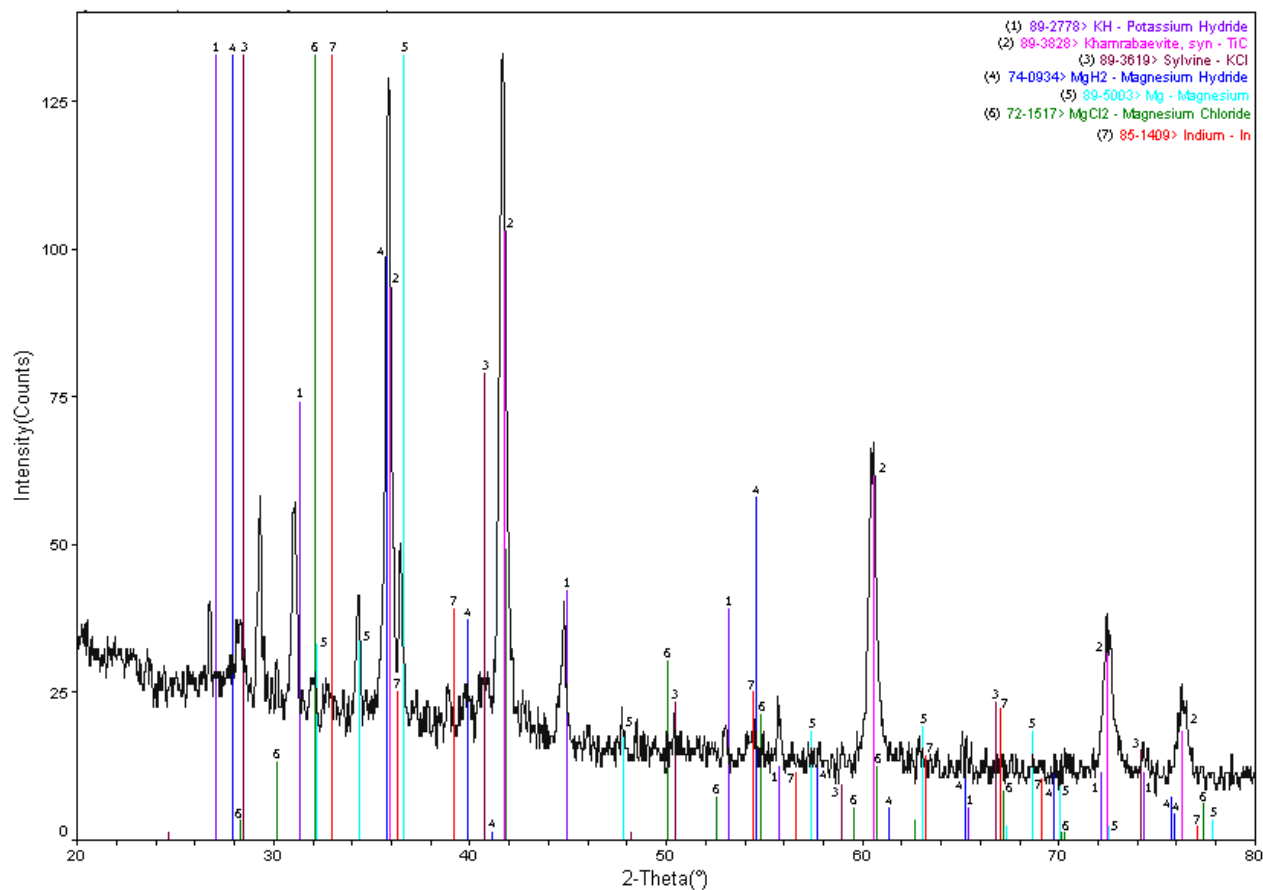


Figure 5. XRD Diffraction patterns of post-reaction sample phase identification at Rowan. Initial reactants included, KH, Mg, TiC and InCl.

### Solution <sup>1</sup>H NMR characterization of post reaction products

Solution <sup>1</sup>H NMR spectrum of post reaction product involving sodium hydride, magnesium, activated carbon and SF<sub>6</sub> gas was extracted in DMF-d<sub>7</sub> solvent for at least 12 hours. Figure 6 shows the <sup>1</sup>H NMR spectra of the solution obtained. A singlet at 8.03 ppm and two quintets centered at 2.92 ppm, and 2.74 ppm are from the solvent. There was a clear additional large upfield shifted peak at -3.85 ppm, which was not due to the solvent. BLP has previously attributed the upfield shifted peaks at -3.85 ppm to H<sup>-</sup>(1/4). This upfield shifted NMR peak had been observed by us, in our compounds in reactions involving hydrogen gas in presence of catalyst and an alkaline salt at high temperature. BLP has attributed this <sup>1</sup>H NMR peak to the formation of hydrido hydride, H<sup>-</sup>(1/4) in the reaction.

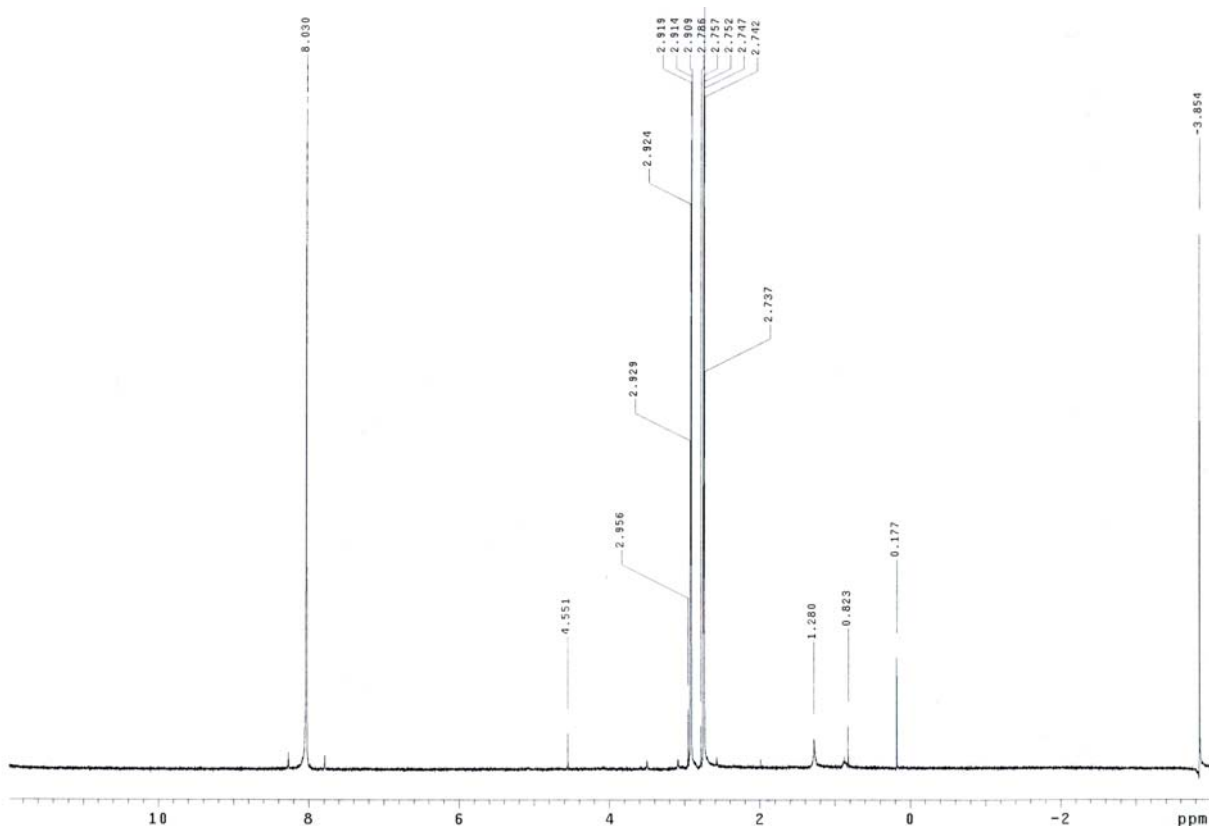
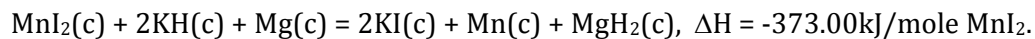


Figure 6. Liquid  $^1\text{H}$  NMR spectrum of an extract of a post reaction sample containing  $\text{NaH}+\text{MgH}_2+\text{SF}_6$ +activated carbon in  $\text{DMF-d}_7$  solvent.

### Energy related discussions

#### Reactions involving manganese iodide, potassium hydride, magnesium and titanium carbide conducted at Rowan.

XRD of the chemical reactions above can help to propose the most probable reaction occurring. It is also possible to estimate the energy accompanying the reaction based on the products observed. The reaction below is the most exothermic known reaction possible.



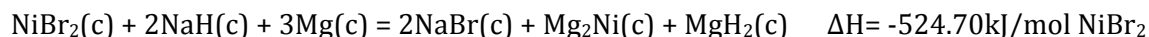
The theoretical maximum conventional chemical reaction energy expected is -373.00 kJ per mole of  $\text{MnI}_2$  [ $\text{MnI}_2$  is the limiting reagent in our trials].

For a 50X reactor, the calorimetric data (061809) showed that 0.5 moles of MnI<sub>2</sub> used generated 336 kJ of energy. This indicates that the energy observed was 1.8 times that theoretically possible by the conventional reaction above.

Three 5X reactors generated 45.0 kJ (062309), 46.8 kJ (062909) and 43.0 kJ (063009) excess energy which translated to 900 kJ/mole, 936 kJ/mole and 860 kJ/mole of MnI<sub>2</sub> respectively. This output is about 2.5 times more than that expected for known reactions. BLP has reported a value of 2.6 times more energy than that from known reactions. To rule out the presence of any oxide/carbonate, careful TPD studies were conducted on MnI<sub>2</sub> and TiC. From the TPD results the amount of water/CO<sub>2</sub>/CO responsible for the formation of oxide/carbonate is negligible (see Appendix C).

**Reactions involving 99% pure nickel bromide (109.5g), sodium hydride (50.0g), magnesium (50.0g) and carbon support (200g) performed at BLP.**

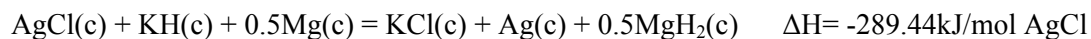
The reaction conducted by BLP-personnel in presence of Rowan staff. For the 50X reaction and based on the products observed, the most exothermic reaction is given below.



The calorimetric data (052909) also showed the energy generated during the reaction was 2.2 times that expected theoretically.

**Reactions involving silver chloride (7.2g), potassium hydride (8.3g), magnesium (5.0g) and activated carbon (20.0g) conducted at Rowan.**

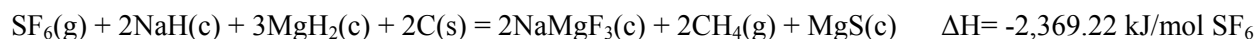
The most exothermic reaction for the 5X reaction based on the products observed, is given below (XRD spectra in Appendix E).



The calorimetric data (070809) also showed that an average of 2.3 times the expected energy was generated.

**Reactions involving sulphur hexafluoride (0.03 mol), sodium hydride (5.0g), magnesium hydride (5.0g) and activated carbon (20.0 g) conducted at Rowan.**

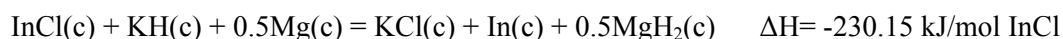
The most exothermic reaction for the 5X reaction based on the products observed, is given below (XRD spectra in Appendix E).



The calorimetric data also showed that an average of 1.2–1.5 times the expected energy was generated.

**Reactions involving potassium hydride (8.3g), magnesium (5.0g), titanium carbide (20g) and indium chloride (7.5g) conducted at Rowan.**

The most exothermic reaction for the 5X reaction based on the products observed, is given below (XRD spectra in Appendix E).



The average calorimetric data showed that an average of 2.05 times the expected energy was generated.

**Reactions involving potassium hydride (7.47g), magnesium (4.5g), titanium carbide (18g) and europium bromide (14.04g) conducted at Rowan.**

The most exothermic reaction for the 5X reaction based on the products observed, is given below (XRD spectra in Appendix E).



The average calorimetric data showed that an average of 6.5 times the expected energy was generated. Based on the XRD results, the corresponding reaction was endothermic, indicating an infinite gain relative to the observed chemical reactions.

**Reactions involving potassium hydride (8.3g), magnesium (5.0g), titanium carbide (20g) and iron bromide (10.8 g) conducted at BLP in the presence of Dr. Peter Jansen.**

For the 5X reaction and based on the products observed, the most exothermic reaction is given below.



The average calorimetric data (062309) showed that an average of 1.84 times more energy than expected was generated.

**Reactions involving potassium hydride (8.3g), magnesium (5.0g), titanium carbide (20g) and cobalt iodide (15.65 g) conducted at Rowan.**

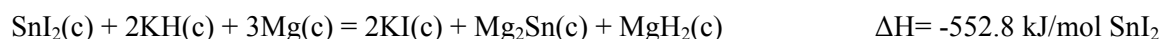
For the 5X reaction and based on the products observed, the most exothermic reaction is given below.



The average calorimetric data (070609) showed that an average of 1.58 times more energy than expected was generated.

**Reactions involving potassium hydride (8.3g), magnesium (5.0g), titanium carbide (20g) and tin iodide (18.5 g) conducted at Rowan.**

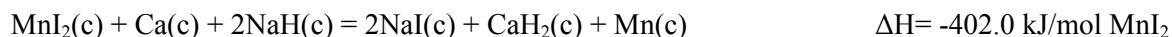
For the 5X reaction and based on the products observed, the most exothermic reaction is given below



The average calorimetric data (071609) showed that an average of 1.66 times more energy than expected was generated.

**Reactions involving sodium hydride (5.0g), calcium (5.0g), activated carbon carbide (20g) and manganese iodide (15.45 g) conducted at Rowan.**

For the 5X reaction and based on the products observed, the most exothermic reaction is given below:



The average calorimetric data (072409) showed that an average of 1.74 times more energy than expected was generated.

## Summary

During the current reporting period we have investigated the chemistry and thermodynamics of the reaction mixtures containing AH (A = Na or K), Mg and , several halides on various supports. The alkali metal hydrides served the dual role of catalyst and hydrogen source. Both metal halides such as, NiBr<sub>2</sub>, MnI<sub>2</sub>, AgCl, EuBr, FeBr<sub>2</sub>, InCl and non-metal halide SF<sub>6</sub> were tested for the reaction. The presence of calcium or magnesium metal powder, the metal halide and a support material were essential for the progress of the reaction. Typically, the reaction mixtures were loaded and heated in a cell to initiate the reaction. All manipulations were carried out in the Ar-filled drybox. The reaction products were characterized initially using XRD. The chemical identity of the products from the XRD studies were used in writing the reaction scheme. In several of the runs the products were mainly magnesium hydride, the metal of the metal halide reactant, and an alkali halide salt. There was no evidence of crystalline metal halide in the final product, indicating its complete consumption. Calorimetric studies indicated the release of energy far in excess of what is predicted based on the elementary thermodynamic calculations. Products of the reaction mixture containing NaH, MgH<sub>2</sub>, activated carbon, and SF<sub>6</sub> indicated the presence of “hydrino” species by use of liquid <sup>1</sup>H NMR.

TPD results on the starting materials indicate that there was no water or oxides of carbon present. The absence of detectable amount of metal oxides in the XRD patterns of the products further rules out the possibility of a reaction between water and reactive metals. Although we have not concluded our work in the area of characterization, the presence of the new forms of lower energy hydrogen “hydrino” observed in our previous report may be responsible for these higher than expected energy gains observed.

In conclusion, the experimental work carried out at Rowan University in the Departments of Engineering and Chemistry confirms independently the empirical findings of BLP with respect to anomalous heat generation and chemical analysis. BLP attributes the anomalous heat generated to the formation of an unusual state of hydrogen during these reactions, what they have named 'hydrinos'.

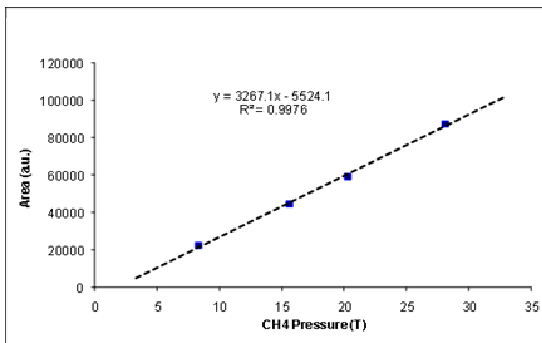
## Appendix Section:

### Appendix A

#### CH<sub>4</sub> Quantification

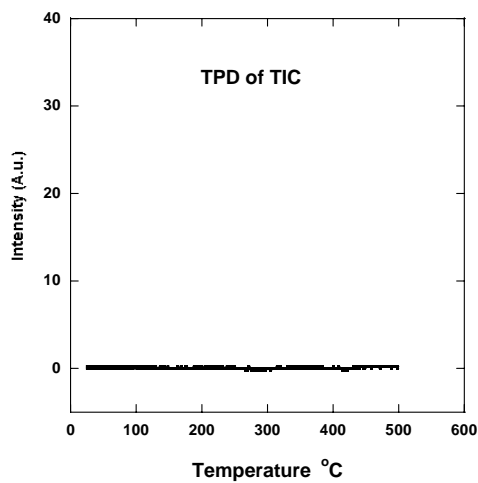
CH <sub>4</sub> Control			
Pressure (T)	Area		
8.3	22882.8		
15.6	44824.7		
20.3	59342.5		
28.1	87405.5		
		y=3267.1x - 5524.1	
P (T)	Area	Calculated Area	%
13.8	6064.4	39561.88	15.33
20.8	10110	62431.58	16.19
		Av:	15.76

CH<sub>4</sub> content in the gas is about 16%.



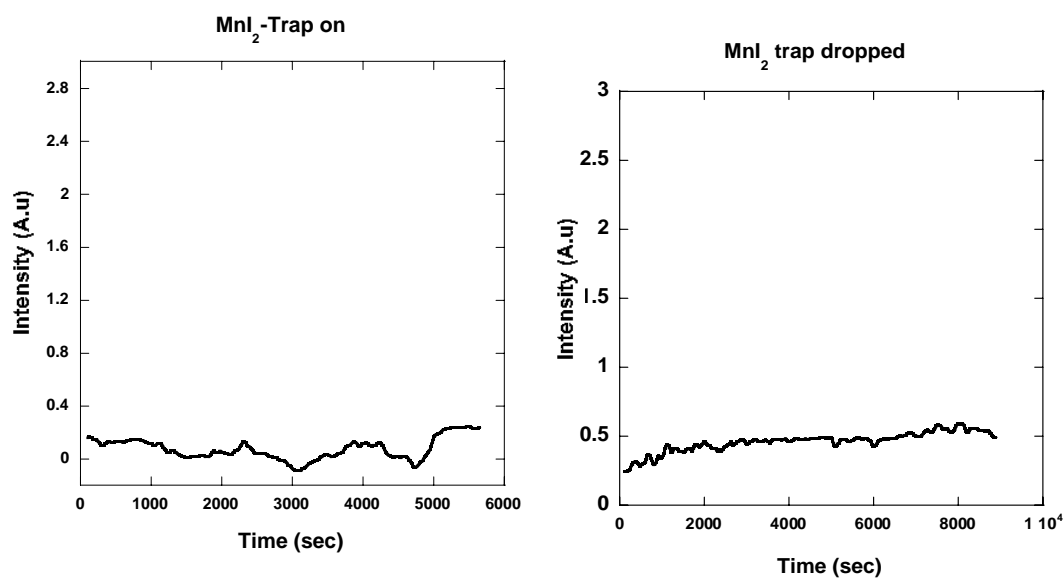
CH<sub>4</sub> calibration: linear relationship of GC responding area vs pressure (with same sampling volume)

### Appendix B



TPD (temperature-program desorption) of TiC

## Appendix C

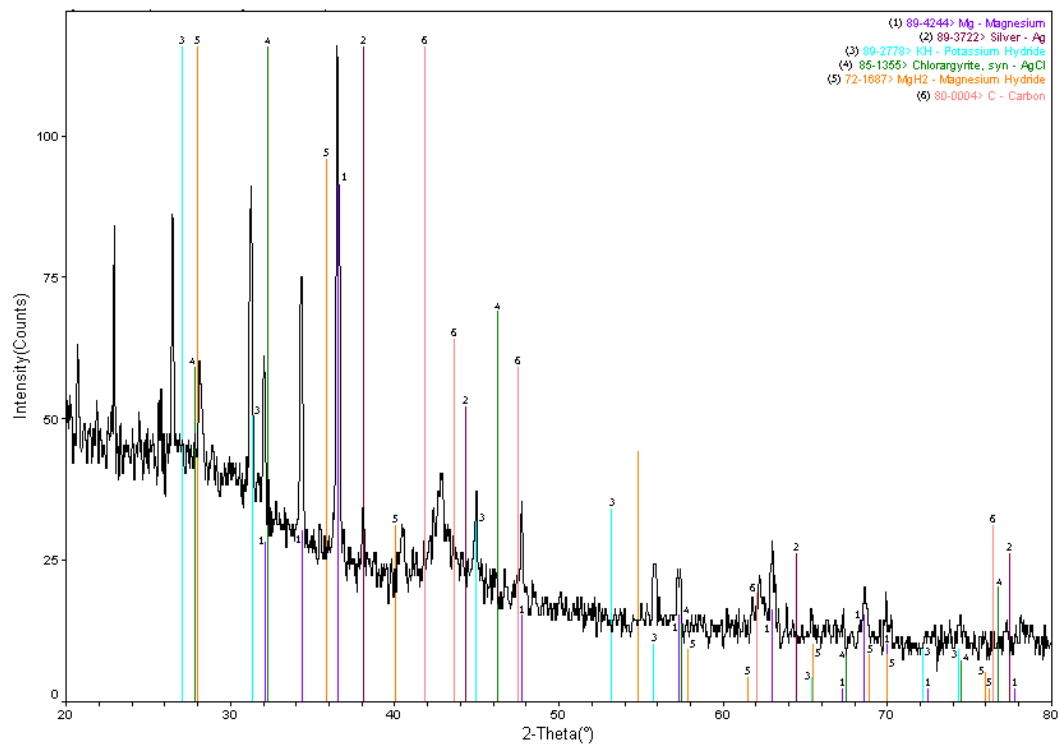


TPD (temperature-program desorption) was performed by trapping gases from heated MnI<sub>2</sub> using a cold trap and then dropping the trap to evaporate the condensed gas.

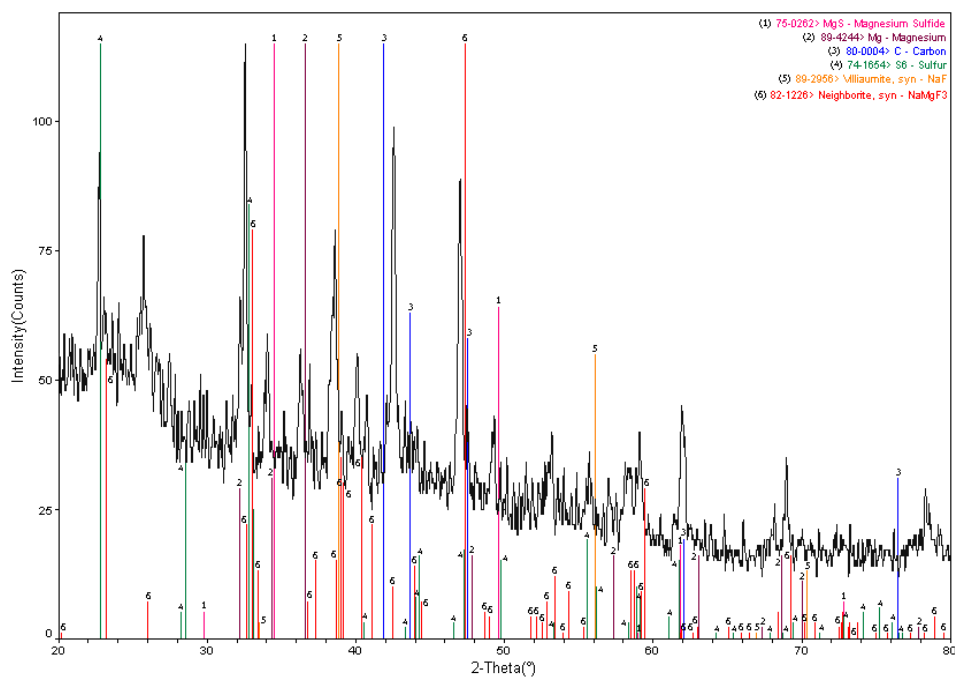
## Appendix D

Sample	RT (oC)	P (T)	Volume (mL)	Weight (g)	N (mole)	N (mole/g)
TiC	23.61	2.37	314.3	0.508	4.025E-05	7.923E-05
MnI <sub>2</sub>	23.4	1.5	314.3	0.54	2.549E-05	4.721E-05

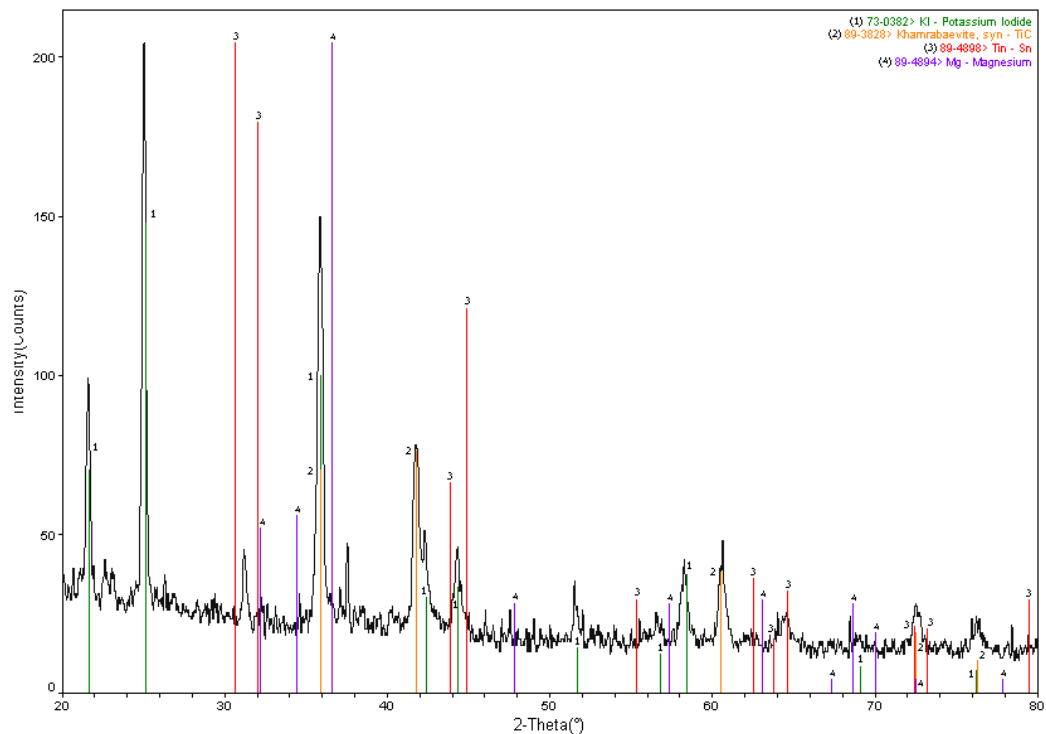
## Appendix E



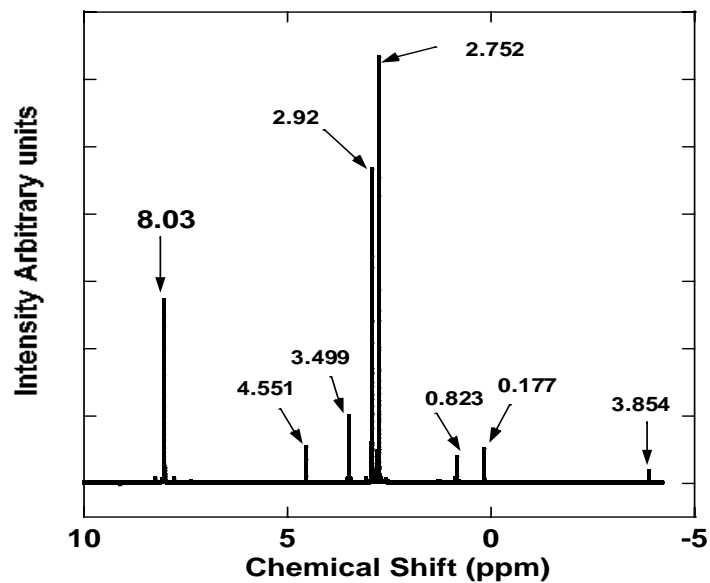
Initial reactants include potassium hydride, magnesium, activated carbon and silver chloride.



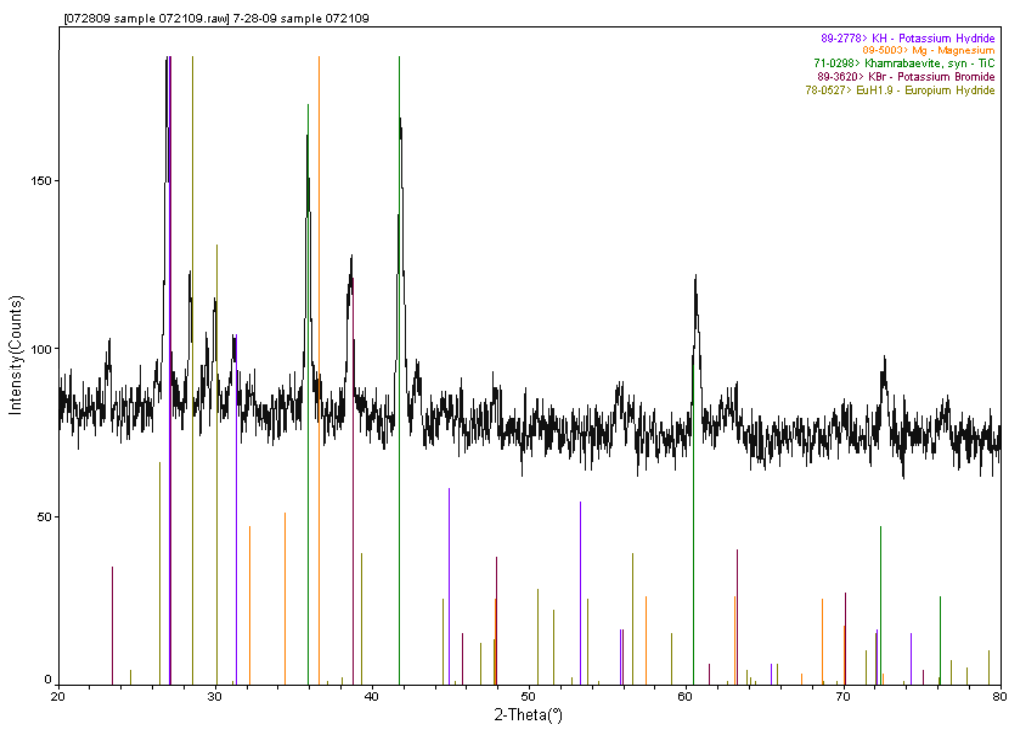
Initial reactants include sodium hydride, magnesium hydride, activated carbon and sulfur (VI) fluoride.



Initial reactants include potassium hydride, magnesium, titanium carbide and tin (II) iodide.



Liquid  $^1\text{H}$  NMR spectrum of an extract of a post reaction sample containing  $\text{NaH} + \text{MgH}_2 + \text{SF}_6 +$  activated carbon in  $\text{DMF-d}_7$  solvent.



aterials Data, Inc. [XRD]chemist\c:\Program Files\Scintag, Inc\datafiles\BLP> Tuesday, Jul 28, 2009 04:31p (MDI\JADEB)

Initial reactants include potassium hydride, magnesium, activated carbon and europium bromide.