# **Supporting Information**

# **Catalytic Ignition of Ionic Liquids for Propellant Applications**

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## I. Materials and Methods

**Chemicals.** 2-Hydroxyethylhydrazine (Fluka) and nitric acid (Fischer) were used as received. De-ionized water (purified with Barnstead Nanopure Lab Water System D4741 (Dubuque, Iowa), was used as solvent. Catalysts studied included: Palladium 5 or 10 wt.% on activated carbon (Aldrich); Samarium 40 mesh, 99% trace metals basis (Aldrich); Iron puriss.,  $\geq$ 99% (manganometric), powder (<150 µm) (Aldrich); W.R. Grace and Co. Raney<sup>®</sup>2800, slurry, in H<sub>2</sub>O (Aldrich); Platinum foil, 1.0 mm, 99.99% trace metals basis (Aldrich); Indium foil, 1.0 mm, 99.999% trace metals basis (Aldrich); Indium foil, 1.0 mm, 99.999% trace metals basis (C3 Propulsion); Stainless Steel, Chromium content  $\geq$ 10 wt.% content by mass (C3 Propulsion). The Shell-405 (20-30 mesh) used was produced by Aerojet at Aerojet's Redmond, Washington facility under the name, "S-405," and is iridium on an alumina support (32% Ir/Al<sub>2</sub>O<sub>3</sub>).

**Thermogravimetric Analysis (TGA).** A TA Instruments (New Castle, DE) model 2950 thermogravimetric analyzer was used. The samples were analyzed on platinum pans with a purge gas of dried air and measured in the dynamic heating regime. Samples between 5-15 mg were heated from 30-600 °C using a constant heating ramp of 5 °C min<sup>-1</sup> with a 30 min isotherm at 75 °C. The isotherm was required to ensure that all water or residual solvent was removed. Long-term stability tests were performed by heating the samples to 75 °C and keeping them at this temperature for 24 h. Decomposition temperatures shown were determined by TGA, heating at 5 °C min<sup>-1</sup> under dried air atmosphere and are reported as (a) onset to 5 wt% mass loss (T<sub>5%dec</sub>) and (ii) onset to total mass loss (T<sub>dec</sub>). Glass transition (T<sub>g</sub>) points (°C) were measured from the transition onset temperature and determined by DSC from the second heating cycle at 5 °C min<sup>-1</sup>, after cooling samples to -100 °C.

**Differential Scanning Calorimetry (DSC).** A DSC 2920 Modulated DSC, TA Instruments, Inc. (New Castle, DE) differential scanning calorimeter was used to determine melting points, glass transitions, and crystallization temperatures. The instrument was temperature calibrated with indium (mp 156.61 °C;  $\Delta H = 28.71 \text{ J g}^{-1}$ ) and DI water before data was collected on IL samples. Data was collected at constant atmospheric pressure using samples between 3-10 mg. Samples were placed in closed aluminum pan (KLD-202, KEtecand Lab Devices, Inc., Mount Berry, GA) perforated with a pin-hole to equilibrate pressure from potential expansion of evolved gases or residual solvents. An empty closed pan was used as a reference. The DSC was adjusted so that zero heat flow was between 0 and -0.5 mW and the baseline drift was less than 0.1 mW over the temperature range of 0-180 °C.

The experimental protocol was as follows. Solid samples (HEH2N) were initially heated to a temperature no greater than 30 °C below the  $T_{5\%dec}$  of the sample, which was predetermined by TGA analysis. Heating was conducted at constant a rate 5 °C /min. After a 5 min isotherm at maximal temperature, samples were cooled to -110 °C. A 5 minute equilibration interval was applied and the entire process was repeated twice (3 cycles total). Liquid samples (HEH, HEHN) were first cooled to -110 °C, and then heated to a temperature no greater that 30 °C below  $T_{5\%dec}$ , previously established by TGA. After a 5 minute equilibration interval, the process was repeated twice (3 cycles total). All transition temperatures were determined from the onset temperatures for the observed melting point, glass, or liquid-liquid transitions.

**Spectroscopy** (NMR/IR). All Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker Avance Spectrometer Bruker/Magnex UltraShield 500 MHz magnet. <sup>1</sup>H NMR measurements were taken at 500 MHz while <sup>13</sup>C NMR measurements were taken at 125 MHz. Data were collected utilizing DMSO- $d_6$  as the solvent with TMS as the internal standard, with chemical shifts in  $\delta$  (ppm). Infrared (IR) spectra were obtained by direct measurement of the neat samples utilizing a Perkin-Elmer Spectrum 100 FT-IR instrument (Waltham, MA) featuring an ATR force gauge (Shelton, CT). IR spectra were obtained in the range of 650 - 4000 cm<sup>-1</sup>.

**Ignition Delay.** A high speed camera, Redlake's MotionPro $\mathbb{R}$  HS 4, was used to determine the ignition delay (ID) times. Fast frame rates with 500 fps (frame per second) at frame resolution of 1280 x 1024 pixels were used. Ignition delay times were determined by counting the frames between the drop of IL first hitting the surface of the catalyst and sign of the first visible ignition.

**Water Content Determination.** Parts per million quantities of water were determined via coulometric Karl Fischer (KF) titration using a Metrohm 684 KF Coulometer from Brinkmann Instruments, Inc. (Westbury, NY). Each sample was titrated three times and if found in good correlation, the values were averaged to obtain the water content.

**Density.** The density of HEHN was determined by mass to volume ratio. Density of each sample was determined five times and if found in good correlation, the values were averaged to obtain the actual density value.

#### **II.** Synthesis

The published acid-base reaction (Scheme 1; Drake, et al.,<sup>1)</sup> was used to prepare 2-hydroxyethylhydrazinium nitrate and 2-hydroxyethylhydrazinium dinitrate.



Scheme 1. Reaction of 2-hydroxyethylhydrazine and nitric acid.

**Hydroxyethylhydrazinium nitrate,** [HO(CH<sub>2</sub>)<sub>2</sub>NHNH<sub>3</sub>][NO<sub>3</sub>] (HEHN). A preweighed 50 mL round bottom flask equipped with a condenser, a teflon stirbar, and a cooling bath was charged with 2-hydroxyethylhydrazine (15 mmol, 1.140 g). Aqueous nitric acid (15.8 M, 15 mmol, 0.95 mL) was added dropwise by means of an addition funnel. Excess heat evolved upon addition was removed via an ice bath. The clear homogenous solution was stirred at ambient temperature overnight (*ca.* 12 h). At the end of this time, the stirbar was removed and the solvent removed by air stream for 12 h, resulting in a colorless, viscous oil. The flask and the viscous product were transferred to a vacuum line and kept under vacuum for another 10 h. The resulting material was additionally dried in a 50 °C furnace, resulting in a viscous, clear oil. Yield: 97.6 %. <sup>1</sup>H NMR (360 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  ppm 6.82 (s, 4H), 3.60 (t, *J* = 5.29 Hz, 2H), 2.98 (t, *J* = 5.33 Hz, 2H); <sup>13</sup>C (360 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  ppm 56.641, 52.641; IR: 3320 (w), 3052 (w), 2891 (w), 1610 (w), 1297 (s), 1154 (m), 1067 (m), 1040 (m), 926 (m), 823 (m). Water content, ca. 8.1 %. Density, 1.423 g/mL.

**Hydroxyethylhydrazinium dinitrate,** [HO(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>NH<sub>3</sub>][NO<sub>3</sub>] (HEH2N). The above procedure was used to prepare HEH2N with the only difference in the amount of nitric acid, added (15.8M, 15 mmol, 1.9 mL). Yield: 98.1 %. <sup>1</sup>H NMR (360 MHz, DMSO-*d*<sub>6</sub>) δ ppm 7.06 (s, 5H), 3.61 (t, J = 5.37 Hz, 3H), 2.98 (t, J = 5.40 Hz, 3H); <sup>13</sup>C (360 MHz, DMSO-*d*<sub>6</sub>) δ ppm 56.641, 52.641. IR: 2884 (w), 264<sub>1</sub> (w), 1613 (w), 1556 (w), 1395 (m), 1280 (s), 1065 (m), 1023 (m), 970 (m), 821 (m). Water content 4.2 %.

<sup>&</sup>lt;sup>1</sup> Brand, A.; Drake, G. W. "Energetic Hydrazinium Salts", U.S. Patent 6218577, issued 17 April 2001.

Table S1.Thermal Analysis Data								
Material	TGA (°C) DSC (°C)		Thermal Stability					
HEH (neutral)	$T_{5\%dec} = 102.10$	T <sub>g</sub> -72.11	- 88.1% weight loss					
	$T_{onset} = 181.98$							
	$T_{dec} = 195.94$							
HEHN	$T_{5\%dec} = 193.63$	$T_g = -56.91$	-23.8% weight loss					
	$T_{onset} = 214.10$							
	$T_{dec} = 259.67$							
HEH2N	$T_{5\% dec} = 62.71$	$T_g = -47.89$	-43.8% weight loss					
	$T_{onset} = 91.51$							
	$T_{dec} = 101.01$							

## III. Thermal analysis data (DSC, TGA)

Decomposition temperatures shown were determined by TGA, heating at 5 °C min-1 under dried air atmosphere and are reported as (a) onset to 5 wt% mass loss ( $T_{5\%dec}$ ); (ii) onset to total mass loss ( $T_{onset}$ ); and (iii) peak temperature ( $T_{dec}$ ). Glass transition (Tg) points (°C) were measured from the transition onset temperature and determined by DSC from the second heating cycle at 5 °C min-1, after cooling samples to - 100 °C. The longer term stability was measured by heating each sample to 75 °C for 24 h.

# IV. Reactions of HEH, HEHN and HEH2N with catalysts.



**Fig S1**. The only catalyst with observable (the formation of bubbles) activity toward HEHN and HEH2N at RT was Shell 405.

**Initial screening for the decomposition reaction of ILs on various metal-based catalysts**. Initial screening for the decomposition reaction of HEHN and HEH2N on various metal-based catalysts (see text). No reaction with any metal was determined except for Shell 405 where the reactions proceeded extremely slowly with only the formation of bubbles to indicate any reaction at all. Virtually all of the mass of sample added remained on the catalyst after ~4 h (Figure S1).

**Decomposition of HEHN and HEH2N on pre-heated Shell 405.** The First Drop Tests in Table 1 of the manuscript refer to addition of each compound to fresh Shell 405 and were followed by subsequent runs on the same catalyst. While the subsequent additions  $(2^{nd} \text{ and } 3^{rd} \text{ drop of IL})$  of the ILs to Shell 405 at 150 °C were monitored with a high speed camera, at other



**Fig. S2.** Example of set-up for the reactions of HEH, HEHN, and HEH2N with preheated Shell 405.

temperatures (50, 100, or 200 °C) subsequent additions were monitored only visually.

Multiple Drop (Catalyst Recycle) Tests at 50, 100, or 200 °C. Approximately 10 min after each first drop test and after reheating each catalyst to the required temperature, a second portion of each compound was added and the results were noted. (This was repeated for the 3rd drop test using the same protocol.) In general, the qualitative results follow those reported above for the addition of the first drop at each temperature; however differences are apparent when considering the data in **Table S2**.

Comp.	<b>Observations</b>	50 °C	100 °C	200 °C
<b>HEH</b> 2 <sup>nd</sup> drop	Observations Residue/Char	No reaction 100%	No smoke, slow bubbling 55%	Smoke evolution, no flame 0%
3 <sup>rd</sup> drop	Observations Residue/Char	No reaction 100%	No smoke, almost no bubbling 94%	Smoke evolution, no flame 0%
<b>HEHN</b> 2 <sup>nd</sup> drop	Observations Residue/Char	No reaction 100%	Visible bubbling observed, with no smoke, no flame 60%	Smoke evolution after delay followed by ignition 0%
3 <sup>rd</sup> drop	Observations Residue/Char	No reaction 100%	Slow bubbling observed, with no smoke, no flame 98%	Smoke evolution, no flame 0%
<b>HEH2N</b> 2 <sup>nd</sup> drop	Observations Residue/Char	No reaction 100%	Smoke evolution, no flame 35%	Smoke evolution after delay followed by ignition 0%
3 <sup>rd</sup> drop	Observations Residue/Char	No reaction 100%	Slow bubbling observed with no smoke, no flame 73%	Smoke evolution after delay followed by ignition 0%

Table S2. Catalyst Recycle Tests at 50, 100, or 200 °C.

At 100 °C, only HEH2N showed any visible reactivity when adding the  $2^{nd}$  drop, but a significant delay was observed before the appearance of any smoke. The  $3^{rd}$  drop of HEH2N to catalyst at this temperature did not appear to react at all. Nonetheless, in all cases at 100 °C an apparent mass loss was found after the reaction. At same temperature, HEHN resulted in only visible bubbling when adding the  $2^{nd}$  drop. HEH itself appeared to be least reactive since no smoke, and extremely slow bubbling were observed at the same conditions.

At 200 °C, catalytic ignition with an observable flame was noted for both HEHN and HEH2N. HEH2N appeared the most reactive with ignition all drops at 200 °C, while HEHN was less reactive, but did demonstrate catalytic ignition at 200 °C with addition of the  $2^{nd}$  portion. Though, no ignition was observed after the  $3^{rd}$  drop and an extended delay was observed before the appearance of a smoke. In comparison, HEH showed no such reactivity toward Shell 405 and appeared to be least reactive since only smoke, and no flame were observed even at 200 °C. The situation was similar with qualitative estimations of delay times. At 200 °C, the delay times decreased in the order HEH > HEHN > HEH2N. In addition, the longevity of smoke evolution increased for all compounds as the  $2^{nd}$  and  $3^{rd}$  drops were added.

Results at 150 °C are similar to those reported here, and are provided in the manuscript. From the obtained results it was concluded that the HEH2N is the most reactive based on the best performance with reused catalyst. Although all three completely decomposed at 100 °C on fresh Shell 405, larger amounts of HEH2N than either HEH or HEHN were decomposed during the second run, at otherwise identical conditions. Similarly, in the third run ~1/4 of the HEH2N was consumed, while both HEH and HEHN were practically unreactive.