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### Flow-Tube Investigations of Hypergolic Reactions of a Dicyanamide Ionic Liquid Via Tunable Vacuum Ultraviolet Aerosol Mass Spectrometry

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#### Abstract

The unusually high heats of vaporization of room-temperature ionic liquids (RTILs) complicate the utilization of thermal evaporation to study ionic liquid reactivity. Although effusion of RTILs into a reaction flow-tube or mass spectrometer is possible, competition between vaporization and thermal decomposition of the RTIL can greatly increase the complexity of the observed reaction products. In order to investigate the reaction kinetics of a hypergolic RTIL, 1butyl-3-methylimidazolium dicyanamide (BMIM<sup>+</sup>DCA<sup>-</sup>) was aerosolized and reacted with gaseous nitric acid, and the products were monitored via tunable vacuum ultraviolet photoionization time-of-flight mass spectrometry at the Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source. Reaction product formation at m/z 42, 43, 44, 67, 85, 126, and higher masses was observed as a function of HNO<sub>3</sub> exposure. The identities of the product species were assigned to the masses based on their ionization energies. The observed exposure profile of the m/z 67 signal suggests that the excess gaseous HNO<sub>3</sub> initiates rapid reactions near the surface of the RTIL aerosol. Non-reactive molecular dynamics simulations support this observation, suggesting that diffusion within the particle may be a limiting step. The mechanism is consistent with previous reports that nitric acid forms protonated dicyanamide species in the first step of the reaction.

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#### **INTRODUCTION**

The emergence of room temperature ionic liquids (RTILs) in the last decade has stemmed mostly from their extremely high enthalpies of vaporization, driving chemical technologies where reduction of vapors is important, such as replacement of volatile organic compounds (VOC) as solvents<sup>1</sup> and highly toxic and volatile liquid propellants.<sup>2-7</sup> Additional interest in RTILs is based on their conductive properties for use as electrolytes in fuel cells<sup>8</sup> and on their high thermal stabilities for high temperature applications such as heat exchange.<sup>9,10</sup> The significant enthalpies of vaporization are due to the ionic nature of the liquids, where the intermolecular attractive Coulombic force is significantly stronger than those found in molecular liquids that are held together by van der Waals, dispersion and possibly hydrogen bonding. Therefore, the energy required to separate ions, ion pairs or clusters of ions from the surface of the ionic liquid is much higher than for molecular liquids. In fact, competition between vaporization of intact RTILs and thermal decomposition to form molecular species that subsequently vaporize can both contribute to mass loss upon heating of RTILs.<sup>11,12</sup>

While it has been previously demonstrated that RTILs can be evaporated intact and introduced into a mass spectrometer (MS) for detection,<sup>13</sup> differentiating between MS signals of the intact RTIL, the thermal decomposition products and molecular impurities in the RTIL is rather difficult. The resulting number densities in the gas phase from the effusive source are quite low, and highly sensitive MS techniques are needed, usually with extensive signal averaging required.

An alternative to effusion sources that has been recently demonstrated<sup>14</sup> is to produce RTIL aerosols, which can be introduced into the MS, flash vaporized and detected via photoionization techniques. Another advantage to this approach is that the RTIL aerosols can be

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reacted with oxidizers and the resulting processed aerosol particles can be probed for product species. Previous attempts to study the reactivity of hypergolic RTILs via supersonic reactive scattering of HNO<sub>3</sub> with a RTIL surface and probing via angle-resolved quadrupole MS resulted in detection only of reactive halide impurities present in the RTILs from their synthesis.<sup>†</sup>

The interest in understanding the hypergolic ignition mechanism of RTILs stems from the desire to improve the performance of the state-of-the-art bipropellants used currently, i.e., monomethylhydrazine and nitrogen tetroxide. It has been estimated that the number of ionic combinations of cations and anions that could potentially be ionic liquids is  $\sim 10^{18}$ .<sup>15</sup> Since it would be impossible to synthesize all of these potential ionic liquids and test them for hypergolicity, understanding the hypergolic ignition mechanisms of RTILs will greatly support the efficient development of next-generation RTIL propellants. Previous work on the hypergolic ignition of dicyanamide (DCA<sup>-</sup>: N $\equiv$ C-N-C $\equiv$ N<sup>-</sup>) based ionic liquids with HNO<sub>3</sub> as the oxidizer indicates the reaction occurs primarily on the anion, proceeding through a high-energy intermediate that is highly thermally unstable and decomposes to create the "chemical spark" needed for ignition.<sup>3</sup> Heat released from the reaction can cause thermal decomposition of the RTIL and oxidizer, and can contribute to the proper conditions leading to ignition. The ignition delay of these RTILs has also been modeled using chemical kinetics modeling.<sup>2</sup> More recently, other hypergolic RTILs have been discovered with different anions (e.g., nitrocyanamides, cyanoborohydrides, aluminoborohydrides, etc.),<sup>6,16</sup> and different oxidizers (primarily H<sub>2</sub>O<sub>2</sub>),<sup>4</sup> or even with hypergolic cations.<sup>17,18</sup>

This paper presents the experimental investigation of the reactivity of dicyanamide-based hypergolic RTIL aerosols with HNO<sub>3</sub> via tunable vacuum ultraviolet (VUV) photoionization time-of-flight mass spectrometry (TOFMS) and discusses how the results give insight into

<sup>&</sup>lt;sup>†</sup>Unpublished work carried out with the Minton Group at Montana State University, Bozeman, MT.

hypergolic reactivity. To our knowledge, this is the first study investigating the reactivity of ionic liquid aerosols. This method could ultimately prove useful in investigating reaction mechanisms for hypergolic combinations with new RTILs and other oxidizers. Non-reactive molecular dynamics simulations indicate that diffusion of HNO<sub>3</sub> within the RTIL aerosol particle may be a limiting factor in hypergolic product formation. Additional insight on the role of  $NO_2^+$  in the hypergolic mechanism of RTILs using FTIR spectroscopy is also discussed.

#### EXPERIMENTAL

The ionic liquid used in these experiments is 1-butyl-3-methylimidazolium dicyanamide, BMIM<sup>+</sup>DCA<sup>-</sup> (98%, EMD Chemicals), which was used without further purification. White fuming nitric acid was synthesized by reacting sulfuric acid (oleum) with sodium nitrate or isotopically-labeled potassium nitrate (K<sup>15</sup>NO<sub>3</sub>, Aldrich: 98 atom % <sup>15</sup>N) and the nitric acid was distilled off from the reaction vessel.

The aerosol reaction kinetics flow-tube apparatus is depicted in Figure 1. The ionic liquid aerosol was generated using solutions of BMIM<sup>+</sup>DCA<sup>-</sup> in deionized water varying in concentration from 0.2 to 4.6 grams per liter and spraying these solutions through an atomizer with 10 psi nitrogen backing pressure.<sup>14</sup> The resulting particles were dried through a 1-meter-long drying tube containing silica gel desiccant, but some residual water likely remains in the aerosols. The resulting ionic liquid aerosol size distributions (Figure 2) were measured using a scanning mobility particle sizer (SMPS), and typical aerosol size distributions ranged from 50 to 500 nm with an optimal peak at 100 nm as determined by controlling the backing pressure in the atomizer. The nitric acid was introduced using a glass bubbler, and the bubbler temperature was maintained at 20 °C in a water bath, yielding 50 Torr of HNO<sub>3</sub>. The HNO<sub>3</sub> concentration was

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monitored by observing the optical absorbance at wavelength,  $\lambda = 213.9$  nm, using an absorbance cell of length = 10.0 cm equipped with a Zn lamp and a photodetector attached to a suitable bandpass filter. An absorption cross section value of  $\sigma_{(HNO3)} = 4.39 \times 10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup> at 213.9 nm was used.<sup>19</sup> The nitric acid was diluted in nitrogen to the appropriate concentrations using a calibrated mass flow controller. The ionic liquid aerosol flow was rapidly mixed with the diluted nitric acid stream and the mixture was flowed through a 1.0-inch-ID Pyrex tube. Reaction times were calculated using the volume of the tube (length = 25 or 50 cm) divided by the total flow (500 cm<sup>3</sup> min<sup>-1</sup>, at STP) through the tube. The resulting [HNO<sub>3</sub>] range was (1-50) x 10<sup>13</sup> molec cm<sup>-3</sup>, while the aerosol number density was fixed at ~ 1 x 10<sup>5</sup> particle cm<sup>-3</sup>. The reaction was quenched at the end of the flow-tube by running the reacted flow through a denuder containing sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) pellets to absorb and neutralize the unreacted nitric acid.

The chemical composition of the aerosols exiting the reactor is measured using a custom built, soft-ionization vacuum ultraviolet aerosol mass spectrometer as described by Gloaguen et al.<sup>20</sup> Briefly, the reactor mixture is sampled through a 500  $\mu$ m orifice coupled to an aerodynamic lens to select aerosol particles  $\geq$  50 nm for the purpose of focusing the particle beam and reducing the gas phase molecular concentration by means of pinhole plates described by Liu et al.<sup>21,22</sup> Subsequently, inside the mass spectrometer, the particles are thermally vaporized on a heated copper block at ~ 115 °C and photoionized by tunable VUV radiation produced by the Chemical Dynamics Beamline at the Advanced Light Source. Mass spectra were taken as scans of the photon energy in the range from 7.4 to 15.0 eV, typically in 0.1 eV steps and averaged for 500,000 repeller pulses, to improve the signal-to-noise ratio of the measured photoionization energy curves of the detected products. A part of the remaining flow exiting the reactor is

sampled by the SMPS to simultaneously determine the particle size distribution (see Figure 2) and number concentration.

Additionally, a rapid-scan Fourier transform infrared spectroscopy apparatus (described previously<sup>3</sup>) was utilized to perform drop tests with mixtures of varying ratios from 0-100 wt% of H<sub>2</sub>SO<sub>4</sub> in HNO<sub>3</sub> onto BMIM<sup>+</sup>DCA<sup>-</sup>. The purpose of mixing H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> is to generate  $NO_2^+$  and investigate the influence of  $NO_2^+$  on the hypergolic reaction. Several drops of the BMIM<sup>+</sup>DCA<sup>-</sup> were put into a cuvette in the apparatus, and the H<sub>2</sub>SO<sub>4</sub>/nitric acid mixtures were introduced by dropping from a syringe into the cuvette containing the BMIM<sup>+</sup>DCA<sup>-</sup>. The IR beam probed the volume directly above the cuvette to record spectra from 500-3850 cm<sup>-1</sup> (4 cm<sup>-1</sup> resolution) every 10 msec.

#### THEORY

#### Ab initio Calculations

Theoretical values of the ionization energy (IE) were determined by calculating the gasphase free energy difference between the cationic and neutral species at 298 K and corrected for zero-point energies using the M06/6-31+G(d,p) level of theory. Condensed phase simulations using the generic ionic liquid model (SMD-GIL),<sup>23</sup> described previously,<sup>11</sup> were performed at the M06/6-31G+(d,p) level of theory to determine the free energy profiles of proposed initial reactions. The SMD-GIL solvent descriptor input parameters used for BMIM<sup>+</sup>DCA<sup>-</sup> as a solvent are e = 11.50, n = 1.4300,  $\gamma = 61.24$ ,  $\Sigma \alpha_2^{H} = 0.229$ ,  $\Sigma \beta_2^{H} = 0.265$ ,  $\varphi = 0.2000$  and  $\psi = 0.0000$ . An estimate of the uncertainty in the calculated values is  $\pm 0.2$  eV for the ionization energies (mean unsigned error) and 7.9 kJ/mol for the SMD-GIL model calculations (average mean unsigned error).<sup>24</sup>

#### **APPLE&P** Molecular Dynamics

To obtain molecular level insight into the factors contributing to the experimental product curves, we conducted atomistic molecular dynamics (MD) simulations of a BMIM<sup>+</sup>DCA<sup>-</sup> film exposed to HNO<sub>3</sub> vapor. The objective of these simulations is to investigate the interplay between the adsorption of HNO<sub>3</sub> vapor to the surface of the RTIL droplet and the diffusion of those molecules inside the droplet. Each system contained 300 RTIL pairs and 100 HNO<sub>3</sub> molecules. In these simulations, the simulation cell dimensions were 35 x 35 x 140 Å with the larger dimension being perpendicular to the RTIL film interface. Simulations were conducted at 333 K. MD simulations utilized the atomistic polarizable APPLE&P force field that has been tuned for description of energetic RTILs and their mixtures with nitric acid.<sup>25</sup> Covalent bond lengths were constrained using the velocity-Verlet form of the SHAKE algorithm.<sup>26</sup> The Ewald summation method was used for treatment of long-range electrostatic forces between partial atomic charges and between partial charges and induced dipoles. A tapering function was used to drive the induced dipole/induced dipole interactions to zero at a cutoff of 10 Å, with scaling starting at 9.3 Å. Induced dipoles were calculated using an iterative procedure at every time step. A cutoff of 10 Å was used for all van der Waals interactions and the real part of electrostatic interactions in the Ewald summation. A multiple time step reversible reference system propagator algorithm<sup>27</sup> was employed. A time step of 0.5 fs was used for bonding, bending, dihedral, and out-of-plane deformation motions, while a 1.5 fs time step was used for non-bonded interactions within a cutoff radius of 6.0 Å. Finally, the non-bonded interactions in the range between 6.0 and 10.0 Å and the reciprocal part of the electrostatic interactions were updated every 3 fs.

#### **RESULTS AND DISCUSSION**

#### Vacuum Ultraviolet Photoionization Time-of-Flight Mass Spectrometry

#### I. Product Identification

Representative mass spectra of the BMIM<sup>+</sup>DCA<sup>-</sup> aerosols alone (black) and upon reaction with HNO<sub>3</sub> (red) at 11.0 and 13.5 eV photoionization energies and 115 °C copper block temperature can be seen in Figure 3. Upon reaction with HNO<sub>3</sub> gas, the BMIM<sup>+</sup>DCA<sup>-</sup> aerosol leads to several product species characterized by m/z 42, 43, 44, 67, 85 and 126. By measuring the photoionization efficiency (PIE) curves and their ionization energy (IE) values, of these peaks, see Figure 4, we have attempted to identify their structures by comparison of their experimental IE values with M06-calculated IE values and literature IE values, if available. Photoion (PI) appearance energies were determined for the major photoions by fitting the PIE curves to the function  $\alpha$ (E-E<sub>0</sub>)<sup>2</sup> near the photoionization threshold, as described previously.<sup>14,28,29</sup> These are reported along with their 298 K calculated (M06/6-31+G(d,p)) adiabatic ionization energies in Table 1.

The formation of melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>, m/z 126) has been seen previously in hypergolic reactivity experiments and in dicyanamide salts thermal decomposition.<sup>30,31</sup> Melamine has a theoretical IE value of  $8.5\pm0.2$  eV (M06) that matches well with our m/z 126 experimental IE value of  $8.7\pm0.2$  eV. Alternative m/z 126 species are discussed in the Supporting Information. Although the melting point of melamine is above 250 °C, it could have a detectable vapor pressure at the copper heater block temperature of 115 °C at reduced pressure of 10<sup>-6</sup> Torr. The melamine cation is also known to fragment to m/z 85,<sup>30</sup> 43 and 42<sup>32</sup> (see Table 1), and this is also discussed further in the Supporting Information.

37 38

39 40

41 42 43

44 45

46 47

48 49 50

51 52

53 54

55 56 57

58 59

60

PI mass

126

85

44

44

43

42

67

PI mass

85

43

42

44

42

43

67

IE (expt., eV)

8.7

10.2

13.2

13.8

11.4

10.3

10.2

AE (expt., eV)

10.2

11.4

10.3

10.5

10.3

11.4

10.2

IE (theo, eV)

8.5

10.0

11.7

10.4

10.3

AE (theo, eV)

11.6

11.96

13.23

10.45

10.6

11.9

11.2

1	
2	
3	Table 1 Distance dust invitation energies (
4	Table 1. Photoproduct ionization energies (
5	
6	REACTION
7	$126 + hv \rightarrow 126^+ + e^-$
8	$85 + hv \rightarrow 85^+ + e^-$
9	$CO_2 + hv \rightarrow CO_2^+ + e^-$
10	$N_2O + hv \rightarrow N_2O^+ + e^-$
11	$HNCO + hv \rightarrow HNCO^+ + e^-$
12	$H_2NCN + hv \rightarrow H_2NCN^+ + e^-$
13	HNCNCN + $hv \rightarrow$ HNCNCN <sup>+</sup> + e <sup>-</sup>
14	
15	DEACTION
16	$\frac{\mathbf{REACTION}}{126 + h_{\mathrm{H}} - \mathrm{H}} = \frac{\mathbf{REACTION}}{126 + h_{\mathrm{H}} - \mathrm{H}} = \frac{\mathbf{REACTION}}{126 + h_{\mathrm{H}} - \mathrm{H}}$
17	$120 + hv \neq n_2 \text{INCINC(IND)} \text{IN} n_2 + \text{INICIN} + e$
18	$126 + hv \rightarrow H_2NCNH + HNCNC(N)NH_2 + e$
19	$126 + hv \rightarrow H_2NCN + (H_2NCN)_2 + e$
20	$85 + hv \rightarrow H_2 NCO' + HNCN + e^2$
21	$85 + hv \rightarrow H_2 NCN^+ + HNCO + e^-$
22	$85 + hv \rightarrow HNCO^+ + H_2NCN + e^-$
23	BMIM <sup>+</sup> DCA <sup>-</sup> + $hv \rightarrow$ BMIM: + HNCNCN <sup>+</sup> + e <sup>-</sup>
24	
25	
26	The formation of evanoures $(m/z)$
27	The formation of cyanourea (m/2 85
28	
29	catalyzed reaction product of dicyanamide a
30	
31	to the water retained in the RTIL aerosol ge
32	
33	

ergies (IE) and appearance energies (AE).

(m/z 85) has been proposed as the product of the acidamide anion and water.<sup>3</sup> and it could occur in this work due osol generation process. Cyanourea has a theoretical IE value of 10.0±0.2 eV (M06) that is consistent with the experimental IE of m/z 85 of 10.2 eV. Alternative m/z 85 species are discussed in the Supporting Information. Fragmentation of the cyanourea cation has also been considered in the Supporting Information.

As the product masses get smaller, the number of possible species is also reduced, making identification less complicated. For m/z 42, the experimental IE value of 10.3±0.2 eV matches very well with that for cyanamine, H<sub>2</sub>NCN (calculated IE value of 10.4±0.2 eV, M06, and literature IE value of 10.4  $eV^{33}$ ), and we identify m/z 42 as cyanamine. M/z 42 alternate species include the closed-shell  $H_2N_2C$  species diazomethane (IE value of 8.999±0.001 eV<sup>33</sup>) and 3-H diazirine (IE value of 10.3 and 10.18±0.05 eV<sup>33</sup>) but 3-H diazirine is highly thermally unstable and is not suspected in this system. Also, ionization of ketene, H<sub>2</sub>C<sub>2</sub>O, with known IE value of 9.617 $\pm$ 0.003 eV,<sup>33</sup> can effectively be eliminated as a possible source for m/z 42. In

order to exclude the formation of m/z 42 as a dissociative photoionization fragment from larger m/z 85 or 126 products, the appearance energies (AEs) of m/z 42 from these larger species were calculated (see Table 1). The calculated value of AE (M06) for m/z 42 resulting from dissociative ionization of cyanourea (m/z 85) is 10.6 eV and the AE from melamine (m/z 126) is 13.2 eV, although any m/z 42 resulting from fragmentation of  $126^+$  would be expected to be significantly less than 10% of the  $126^+$  peak intensity when compared to the electron-impact ionization (~ 70 eV) mass spectrum of melamine.<sup>32</sup> The experimental value of 10.3 eV is less than the 10.6 eV AE of m/z 42 from fragmentation of cyanourea. On the other hand, cyanourea can thermally decompose to H<sub>2</sub>NCN + HNCO with a thermal decomposition onset temperature of T<sub>dec</sub> = 100 °C.<sup>34</sup> However, with the copper heater block temperature = 115 °C at ~ 10<sup>-6</sup> Torr pressure, evaporation of cyanourea would be expected to be more significant than thermal decomposition, but we cannot entirely eliminate the latter possibility as a source for m/z 42 (with 10.4 eV M06 IE value).

Previous hypergolic ignition experiments indicate the formation of HNCO (m/z 43) as evidenced by IR spectroscopy,<sup>3</sup> and the appearance of m/z 43 in the reaction of BMIM<sup>+</sup>DCA<sup>-</sup> aerosols + HNO<sub>3</sub> supports this. The experimental IE value for m/z 43 is 11.4±0.2 eV, and while the theoretical IE value (M06) is slightly higher at 11.7±0.2 eV, the literature value is known to a high degree of accuracy to be at an IE value of 11.595±0.005 eV,<sup>35</sup> which matches reasonably well with the experimental value. In addition, the shape of the PIE curve is very similar to the literature photoelectron spectrum.<sup>35</sup> Attempts were also made to identify possible dissociative photoionization fragmentation of the m/z 85 and m/z 126 species as sources for m/z 43 using M06 methods (see Table 1) and by examining the PIE curves carefully to look for features that

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could be resolved and demonstrate fragmentation is occurring. Unfortunately, the signal-tonoise ratio in the measured m/z 43 signal was not sufficient to discern this.

The experimental photoion appearance energy of m/z 67 has a value of  $10.2\pm0.2$  eV, and, as seen in Table 1, the M06 IE of the protonated DCA (HDCA = HNCNCN) has a value of  $10.3\pm0.2$  eV, which suggests that the m/z signal is from HDCA. (Species like C<sub>5</sub>H<sub>7</sub> with much lower IE values are ruled out as alternate candidates for m/z 67 as were C<sub>4</sub>NH<sub>5</sub> and C<sub>3</sub>HNO.<sup>33</sup>)

By reacting BMIM<sup>+</sup>DCA<sup>-</sup> aerosols with isotopically labeled H<sup>15</sup>NO<sub>3</sub>, the expected products - as predicted by the hypergolic reaction mechanism<sup>3</sup> - at m/z 44, namely CO<sub>2</sub> and N<sub>2</sub>O, can be separated, as the isotopically labeled product  ${}^{15}N{}^{14}NO$  appears at m/z 45, as seen in Figure 5. Alternately, the contribution to the m/z 44 peak could be separated by increasing the resolution of the light source by reducing the slit size the light passes through. High-resolution PIE curves for pure  $CO_2$ , pure  $N_2O_2$  and a mixture of  $CO_2/N_2O$  gases leaked into the MS for calibration purposes can be seen in Figure 6. Note that the CO<sub>2</sub> peak centered at 13.5 eV can be baseline-resolved from the N<sub>2</sub>O peak centered at 14.3 eV. The separation of CO<sub>2</sub> and N<sub>2</sub>O at high resolution allows for the measurement of the CO<sub>2</sub> and N<sub>2</sub>O yields as a function of HNO<sub>3</sub> exposure. The overall proposed hypergolic reaction mechanism is:  $[N(CN)_2]^2 + 4HNO_3 \rightarrow 2CO_2$  $+ 3N_2O + 2H_2O + NO_3$  with a ratio of  $N_2O/CO_2 = 3/2$  for the complete reaction. The CO<sub>2</sub> and  $N_2O$  response curves as a function of HNO<sub>3</sub> exposure can be seen in the Supporting Information. Although the shapes of the response curves are consistent with each other and with those of m/z42, 43, 85 and 126, the intensity ratio of the N<sub>2</sub>O/CO<sub>2</sub> response of approximately 5:1 does not match the 3/2 ratio mentioned above, likely due to interferences from other photoion fragments such as from fragments of m/z 85 and m/z 126. Unfortunately, due to this, we cannot get an accurate stoichiometric ratio from this data.

#### II. Species Profile

The decay of HDCA (m/z 67) signal as a function of HNO<sub>3</sub> exposure was investigated to determine the second order rate coefficient for the reaction of DCA<sup>-</sup> with HNO<sub>3</sub>. A detailed analysis of this work is presented in the Supporting Information. Also, an attempt to vary aerosol particle size to vary surface area to volume (SA/V) was made in order to see how the decay of m/z 67 signal is impacted with exposure. The aerosol size distribution as measured by the average particle diameter was able to be varied from ~ 110 nm to ~ 150 nm by varying the backing pressure and the RTIL concentration in the solution in the aerosol generator, yielding a relative difference in SA/V of 27%. However, this was not significant enough to detect changes in the shapes of the exposure curves for m/z signals for HDCA, CO<sub>2</sub>, N<sub>2</sub>O, etc. An alternate method to generate RTIL aerosols of highly varied sizes or to select monodisperse portions of the aerosol distributions of different radii would be beneficial to investigate the impact on the proposed kinetics mechanism.

#### **Molecular Dynamics Modeling**

Initially, the systems were equilibrated with repulsive biasing interactions that prevented aggregation of HNO<sub>3</sub> in the gas and its adsorption onto the RTIL film. As the RTIL liquid interface and the HNO<sub>3</sub> gas phase have equilibrated the biasing potential was turned off, and processes of HNO<sub>3</sub> adsorption and diffusion through RTIL film were monitored as seen in Figure 7. Figure 8 shows the density profiles illustrating molecular distributions in the system for several timeframes. As expected, the density profiles of the RTIL phase (illustrated by the density of BMIM<sup>+</sup> cations) are barely changing upon interaction with HNO<sub>3</sub> gas. However, the density profiles of HNO<sub>3</sub> show more significant changes. First, one can observe that within 20

ps a pronounced peak in the HNO<sub>3</sub> density has developed at the interface with RTIL, indicating rapid adsorption of HNO<sub>3</sub> molecules that were in the vicinity of the RTIL film. Interestingly this peak remains strong after 4 ns and 6 ns of simulations. The figure illustrates that diffusion of HNO<sub>3</sub> through RTIL film is relatively slow. A region of low HNO<sub>3</sub> can be observed in the middle of the RTIL film even after 6 ns of simulations. We would like to point out that in our previous MD simulation study of liquid-liquid mixing of the same RTIL and HNO<sub>3</sub> using similar sized RTIL film, complete intermixing of HNO<sub>3</sub> and RTIL phase had occurred after 6 ns of simulation.<sup>25</sup> In contrast, gas interpenetration appears to be much slower in the simulations, likely due to the much lower concentration gradient in the gas-liquid system. This result is consistent with other experimental observations of solubility of gases like CO<sub>2</sub> in ionic liquids, where the diffusion coefficient is found to be 1-2 orders of magnitude smaller than that in molecular liquids.<sup>36</sup> Hence, it is likely that much of the reaction, e.g., protonation of DCA, and subsequent reactions leading to product formation would occur near the surface; For 150-nm particles, this surface depth varies from 8 to 30 nm, respectively, for S=0.28 and 0.78, where S is the (outer) fractional volume of the total RTIL particle volume that is available for HNO<sub>3</sub> reaction to take place, when the corresponding  $(k_{decomp}/(k_{decomp}+k_{vap}))$  values where 0.1 and 0.9, as discussed in the Supporting Information. For 110-nm particles, the corresponding depth varies from 6 to 22 nm. Therefore, the measured phenomenological rate coefficient  $k_2 = 4.14 \pm 0.32$  x  $10^{-16}$  molec<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup> (see Supporting Information for how this value was obtained) would have contributions from both the intrinsic reaction rate and HNO<sub>3</sub> diffusion rate within the aerosol. The rate coefficient  $k_2$  is expected to be independent of the diffusion rate of gaseous HNO<sub>3</sub> onto the particle surface, which is fast, with an equivalent rate coefficient calculated to be  $\sim 1.2 \times 10^{-10}$ <sup>11</sup> molec<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup> for our experimental flow-tube conditions.<sup>37</sup> The heterogeneous nature of this

system and the phobic behavior of the very dissimilar HNO<sub>3</sub> solute in the BMIM<sup>+</sup>DCA<sup>-</sup> solvent appear to have contributed to the observed m/z product profiles. Previous studies on aerosol/gas reactions have also observed interfacial reactivity behavior; where the reaction is either limited at the surface face or is limited by the slow diffusion of the gaseous reactant into the aerosol particle, and our results appear to rule out rapid diffusion within the RTIL so that [HNO<sub>3</sub>] would be constant throughout.<sup>38</sup> The competing forces which ultimately control the HNO<sub>3</sub> diffusion rate and distribution within the aerosol particle likely include particle surface energy and chemical potential, and diffusion cannot be simply described as driven by the entropy of mixing.

#### **Generic Ionic Liquid Model**

In a recent paper, it was proposed that the relative acidity of HNO<sub>3</sub> and HDCA would reverse from the gas phase to the condensed phase in the ionic liquid.<sup>11</sup> This was simulated using the so-called generic ionic liquid (SMD-GIL) model.<sup>23</sup> In the gas phase, a proton would favor binding with NO<sub>3</sub><sup>-</sup> over DCA<sup>-</sup>, but in the simulated condensed phase, the proton would prefer binding to the DCA<sup>-</sup>. This has important implications in the hypergolic reaction, as proton transfer from HNO<sub>3</sub> to DCA<sup>-</sup> has been proposed as the initial step in hypergolic ignition.<sup>3</sup> In light of this, it is informative to estimate the equilibrium constant, K<sub>eq</sub>, in the condensed phase for the reaction: HNO<sub>3</sub> + DCA<sup>-</sup>  $\leftrightarrow$  NO<sub>3</sub><sup>-</sup> + HDCA using the relationship  $\Delta G^{\circ} = -RTlnK_{eq}$ . The SMD-GIL  $\Delta G^{\circ}_{acid}$  values for the reactions, HNO<sub>3</sub>  $\rightarrow$  H<sup>+</sup> + NO<sub>3</sub><sup>-</sup> and HDCA  $\rightarrow$  H<sup>+</sup> + DCA<sup>-</sup> are 566.6 and 578.0 kJ/mol, respectively. The average mean unsigned error for thermochemical kinetics using M06 is 7.9 kJ/mol. Combining these reactions gives an overall SMD-GIL  $\Delta G^{\circ}_{rxn}$ = -11.4 kJ/mol for the reaction HNO<sub>3</sub> + DCA  $\leftrightarrow$  NO<sub>3</sub><sup>-</sup> + HDCA, yielding a value of K<sub>eq</sub> = 97, indicating the forward reaction is highly preferred over the reverse reaction:

The proposed<sup>3</sup> second and third steps in the hypergolic ignition reaction were the nucleophilic attack of  $NO_3^-$  on the protonated DCA, followed by  $NO_2$  migration to the terminal nitrogen. The enthalpy profile for this mechanism has been calculated recently at the B3LYP/aug-cc-PVDZ and MP2/6-311++G(d,p) levels of theory in the gas phase.<sup>39</sup> The enthalpies and free energies for the first three steps of the mechanism are calculated here using the M06/6-31+G(d,p) and SMD-GIL methods using the input geometries from Ref 39 and the resulting free energy diagram can be seen in Figure 9 (298 K, 1 atm). Here, the proton transfer from the HNO<sub>3</sub> to DCA<sup>-</sup> is exoergic by 11.4 kJ/mol. The subsequent NO<sub>3</sub><sup>-</sup> nucleophilic attack on the HDCA is endoergic by 59.0 kJ/mol (+47.6 kJ/mol relative to reactants) with a free energy barrier of  $\Delta G^{\ddagger} \leq 89.7$  kJ/mol (+78.3 kJ/mol relative to reactants). This free energy barrier is assigned as an upper limit due to the tendency of the SMD-GIL/M06 method to return to geometry 2A (Ref 39) rather than converge to a transition state (i.e., the free energy was determined by fixing the geometry and performing a frequency calculation (freq, Gaussian-09),<sup>40</sup> to yield the upper limit to the free energy of the transition state and a single imaginary frequency corresponding to the nucleophilic attack on the carbon, which was confirmed by internal reaction coordinate analysis). The next step in the proposed mechanism, the migration of  $NO_2$  from the C-O oxygen to the terminal nitrogen, has a calculated free energy barrier of 76.5 kJ/mol and the product formed is highly exoergic with a reaction free energy of -152.9 kJ/mol for this step.

Although the mechanism depicted in Figure 9 proceeds through a series of anionic species, the reactions proposed in Equations (1) and (2) in the Supporting Information imply reactions between neutral species. SMD-GIL free energy calculations for the neutral reactions were also explored and reported here (Figure 10). While the relative free energy of the

stationary state of the nitrated, protonated-dicyanamide species (40.1 kJ/mol) and the free energy barrier for the nitro migration ( $\Delta G^{\ddagger} = 59.5$  kJ/mol, +99.6 kJ/mol relative to reactants) are lower in value than that for the corresponding species in the anionic mechanism (Figure 9), the overall free energy release for this process is also substantially less (-39.2 vs -105.3 kJ/mol) relative to the reactants. Figure 11 shows the free energy profile resulting due to proton transfer to the terminal nitrogen on the HDCA. A search for the transition state for the nucleophilic attack of NO<sub>3</sub><sup>-</sup> on the diprotonated dicyanamide (similar to the first transition state in Figure 9) was unsuccessful and is not included in Figures 11 and 12. It should be noted that previous work<sup>11</sup> indicated that species with ionic character are solvated more readily in the highly polar ionic liquid medium, whereas neutrals or species with little ionic character are solvated less, resulting in potentially significant differences in the SMD-GIL mechanism versus the corresponding gas phase mechanism, for example the reverse in free energies of acidity for HDCA and HNO<sub>3</sub> as mentioned earlier.

The recent work by Nichols and coworkers also investigated the contribution of a second HNO<sub>3</sub> molecule (acting as a spectator) on the reaction in order to determine the possible solvation effect on the (gas-phase) energy profile.<sup>39</sup> The addition of a second HNO<sub>3</sub> molecule has a strong stabilizing effect, which lowers the enthalpies of all intermediates and transition states below the energy of the reactants. These calculations were repeated here using the input geometries from the Supplemental Information from Nichols' work, shown in Figure 12. In contrast to the gas phase calculations, using the condensed phase SMD-GIL model, the addition of a second, neutral HNO<sub>3</sub> molecule has a destabilizing effect on the DCA<sup>-</sup>-HNO<sub>3</sub> adduct relative to the anionic route in Figure 9 of -2.4 – (-18.7) = +16.3 kJ/mol. This could perhaps be explained if the additional, neutral HNO<sub>3</sub> perturbs the solvation shell of the polar ionic liquid

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solvent surrounding the anionic DCA<sup>-</sup>-HNO<sub>3</sub>, thereby destabilizing the DCA<sup>-</sup>[HNO<sub>3</sub>]<sub>2</sub> relative to DCA<sup>-</sup>-HNO<sub>3</sub>.

The differences in the Nichols results (enthalpies) and our results (free energies) indicate that there is a significant entropic contribution to the reaction profile. Therefore, we report the Gaussian calculated (1 atm, 298 K) enthalpy ( $\Delta H^{\circ}$ ), free energy ( $\Delta G^{\circ}$ ) and entropy ( $T\Delta S^{\circ}$ ) contributions for both the gas phase (M06) and for the condensed phase (SMD-GIL) in order to better understand the reaction energetics involved (see Supporting Information, Table S3). The  $\Delta$ H° values determined by M06 for the addition of both one and two HNO<sub>3</sub> molecules have similar trends to those in Ref 39 and the enthalpies match reasonably well. However, due to the entropy loss in combining two or three molecules into one adduct, the  $-T\Delta S^{\circ}$  entropic contributions can shift the energetics of the products higher relative to the reactants. For the addition of one HNO<sub>3</sub> molecule to DCA<sup>-</sup>, the average M06 gas phase shift due to  $-T\Delta S^{\circ}$  is +11.3 kcal/mol (47.2 kJ/mol), and for the addition of two HNO<sub>3</sub> molecules to DCA<sup>-</sup>, the average M06 gas phase shift due to  $-T\Delta S^{\circ}$  is +22.5 kcal/mol (94.1 kJ/mol), which largely tends to cancel out the potential solvation effect of addition of a second HNO<sub>3</sub> molecule (see Table S3 in the Supporting Information). In fact, in the SMD-GIL condensed phase, there is almost no difference in the free energy profiles for one or two HNO<sub>3</sub> molecules as seen in Table S3 of the Supporting Information.

The overall energetics in Figure 9 indicate that the proton transfer from HNO<sub>3</sub> to DCA<sup>-</sup> is exoergic, the subsequent nucleophilic addition of  $NO_3^-$  is endoergic with a barrier, there is a barrier for the NO<sub>2</sub> migration and the NO<sub>2</sub> migration reaction is highly exoergic. This sequence of reactions is consistent with Figure 10 and with the experimental kinetics results in this paper, and it is possible that the NO<sub>2</sub> migration is the rate-limiting step in the hypergolic ignition

mechanism. The energy release of  $NO_2$  migration could lead to the temperature increase observed in the hypergolic ignition of BMIM<sup>+</sup>DCA<sup>-</sup> + HNO<sub>3</sub>. The entropic contributions to the reaction energetics is significant, and these should be included when describing the reaction profile as the free energy of reaction.

#### **Rapid-scan Fourier Transform Infrared Spectroscopy**

The well-known acid-catalyzed catalyzed conversion of nitriles to amides proceeds via protonation on the nitrile nitrogen followed by nucleophilic addition of water to the nitrile carbon and finally ends with proton migration from water to the terminal nitrogen:



In the proposed hypergolic ignition reaction mechanism, an analogous reaction to the acidcatalyzed conversion of nitrile to amide via nucleophilic addition of  $NO_3^-$  followed by  $NO_2$ migration to the terminal N in the dicyanamide occurs (see Figure 9).





The presence of water in the system would compete as a nucleophile with  $NO_3^-$ , leading to the formation of the isocyanoureate (Equation 1). In order to investigate the contribution of the isocyanoureate species in the hypergolic ignition mechanism, separate rapid-scan FTIR drop tests with HNO<sub>3</sub> and BMIM<sup>+</sup>DCA<sup>-</sup> and sodium isocyanoureate were performed, and the results are seen in Figure 13. While the dicyanamide leads to the formation of  $CO_2$ , HNCO and  $N_2O$  as seen in the previous ignition testing, reaction of HNO<sub>3</sub> with the isocyanoureate only leads to the formation of  $CO_2$  and does not yield the HNCO and  $N_2O$  species needed to lead to ignition. This would explain the high sensitivity of ignition delay time to the presence of water in the system, either in the HNO<sub>3</sub> or in the ionic liquid fuel.

One suspected reactive intermediate in the hypergolic ignition mechanism of  $BMIM^+DCA^- + HNO_3$  is  $NO_2^+$ . The investigation into the sensitivity of ignition delay time to  $NO_2^+$  concentration utilized the commonly used nitration chemistry:

$$HNO_3 + 2 H_2SO_4 \leftrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$
(5)

It is well-known and widely utilized in nitration reactions that the addition of  $H_2SO_4$  to  $HNO_3$  can shift the equilibrium in favor of  $NO_2^+$  between about 80-90%  $H_2SO_4$  in  $HNO_3$ . The ratio of  $H_2SO_4$  to  $HNO_3$  was varied in steps of 10 wt%, and the results were measured as a function of the normalized ratio of  $N_2O$  to  $CO_2$  (peak areas), versus increasing  $H_2SO_4$  percent, seen in Figure 14a below. As the concentration of nitrate decreases, the  $N_2O/CO_2$  ratio also decreases. Ignition is observed between 0-60%  $H_2SO_4/HNO_3$ , and although no ignition is observed between 70-88%  $H_2SO_4/HNO_3$ , reaction is observed in the form of smoke evolution above the cuvette. Above 88%, no reaction is observed. Superimposed on the graph in Figure 14b is the normalized  $NO_2^+$  concentration versus  $H_2SO_4/HNO_3$  ratio, and the shift towards  $NO_2^+ + 2HSO_4^- + H_3O^+$  products is essentially coincident with the loss of hypergolic reactivity. This result would imply that  $NO_2^+$  is not an active species in the hypergolic ignition mechanism for dicyanamide-based RTIL + HNO\_3.

The use of the nitration reaction was further utilized to see if the isocyanoureate could be converted back to a reactive species, and a series of drop tests with high  $H_2SO_4/HNO_3$  ratios (in the range where  $NO_2^+$  would be favored) and sodium isocyanoureate were performed, and the results are seen in Figure 15. At 85 wt%  $H_2SO_4/HNO_3$ , approximately the middle of the  $NO_2^+$  curve seen in Figure 14b, a vigorous reaction is observed and the re-emergence of  $N_2O$  appears in the IR spectrum (Figure 15b). This implies that the conversion back to nitroisocyanoureate can promote reactivity, which would be consistent with the originally proposed ignition mechanism:



Lastly, the sensitivity of the ignition to the presence of  $N_2O$  should be noted, as  $N_2O$  could accelerate oxidation and combustion in the ignition process.

#### CONCLUSIONS

In this paper, we demonstrate the ability of aerosol generation coupled with tunable VUV photoionization mass spectrometry to identify many of the products of the reaction of a hypergolic dicyanamide-based ionic liquid with HNO<sub>3</sub>, such as CO<sub>2</sub>, N<sub>2</sub>O and HNCO, and is consistent with the previously proposed reaction mechanism. To our knowledge, this is the first study on the chemical reactivity of ionic liquid aerosols. Measurement of the product profiles as a function of HNO<sub>3</sub> exposure allows for insight into the kinetics of the initial reaction steps in the hypergolic reaction of BMIM<sup>+</sup>DCA<sup>-</sup> + HNO<sub>3</sub>. Kinetics analysis indicates the initial reaction of BMIM<sup>+</sup>DCA<sup>-</sup> with HNO<sub>3</sub> is much faster than the subsequent reaction of HDCA with HNO<sub>3</sub>, and that the reactivity is limited to near the surface of the aerosol particle. Non-reactive molecular dynamics simulations support the idea that the HNO<sub>3</sub> diffusion is slow in the particle and that reactivity would be limited to regions near the surface of the aerosol particle. Additional FTIR experimental results indicate that NO<sub>2</sub><sup>+</sup> appears not to be an important species in the hypergolic ignition mechanism.

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**Figure 1.** Schematic of the BMIM<sup>+</sup>DCA<sup>-</sup> aerosol +  $HNO_3$  reaction kinetics flow-tube setup. The denuder is filled with  $Na_2CO_3$  that removes and neutralizes  $HNO_3$ , effectively ending the reaction.

• 0.2 g/L

▲ 0.5 g/L

4.3 g/L







**Figure 3.** VUV photoionization TOFMS spectra of BMIM<sup>+</sup>DCA<sup>-</sup> + HNO<sub>3</sub> at a) full spectrum, 11.0 eV and b) m/z 40-48, 13.5 eV (CO<sub>2</sub> PIE maximum).



**Figure 4.** Photoionization efficiency (PIE) curves for m/z 42, 43, 44, 67, 85 and 126, with IE of 10.3±0.1, 11.4±0.3, 10.5±0.3, 10.2±0.2, 10.2±0.2 and 8.7±0.2 eV, respectively.



**Figure 5.** Mass spectra at photoionization energy of 14.4 eV between m/z 40-50 for a)  $BMIM^+DCA^- + HNO_3$  and b)  $BMIM^+DCA^- + H^{15}NO_3$ .



Figure 6. High resolution PIE curves for N<sub>2</sub>O, CO<sub>2</sub> and a 1:1 mixture of CO<sub>2</sub> to N<sub>2</sub>O.



**Figure 7.** Snapshots from simulations of BMIM<sup>+</sup>DCA<sup>-</sup> liquid/HNO<sub>3</sub> gas interface: initial (top) and after 6 ns of simulation (bottom).



**Figure 8.** Density profiles for BMIM<sup>+</sup> cations (top) and HNO<sub>3</sub> (bottom) after 20 ps, 4 ns and 6 ns of mixing.



**Figure 9.** Free energy diagram of the reaction of  $HNO_3$  with the DCA<sup>-</sup> anion in the condensed phase calculated by SMD-GIL/M06/6-31+G(d,p). Units in kJ/mol.



**Figure 10.** Free energy diagram of the reaction of  $HNO_3$  with HDCA in the condensed phase calculated by SMD-GIL/M06/6-31+G(d,p), resulting in the proton transfer to the central nitrogen on the HDCA. Units in kJ/mol.



**Figure 11.** Free energy diagram of the reaction of  $HNO_3$  with HDCA in the condensed phase calculated by SMD-GIL/M06/6-31+G(d,p), resulting in the proton transfer to the terminal nitrogen on the HDCA. Units in kJ/mol.



**Figure 12.** Free energy diagram of the reaction of  $2 \text{ HNO}_3 + \text{HDCA}$  in the condensed phase calculated by SMD-GIL/M06/6-31+G(d,p). The second HNO<sub>3</sub> molecule is hydrogen bonded throughout the reaction and acts largely as a spectator. Units in kJ/mol.



**Figure 13.** FTIR spectra of (left)  $BMIM^+DCA^- + HNO_3$  and (right) sodium isocyanoureate +  $HNO_3$ . Note the absence of formation of HNCO and N<sub>2</sub>O from the sodium isocyanoureate.



**Figure 14.** a) FTIR spectra of CO<sub>2</sub> and N<sub>2</sub>O as a function of %HNO<sub>3</sub>, b) N<sub>2</sub>O/CO<sub>2</sub> ratio (left axis) and NO<sub>2</sub><sup>+</sup> concentration (solid curve, normalized, right axis) as a function of H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> ratio in hypergolic drop tests. As the H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> ratio increases, the N<sub>2</sub>O/CO<sub>2</sub> ratio decreases until 70% H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>, where ignition is quenched. Where the NO<sub>2</sub><sup>+</sup> concentration increases - between 80 and 90% H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>- the hypergolic reactivity stops, indicating that the presence of NO<sub>2</sub><sup>+</sup> suppresses hypergolic reactivity.



**Figure 15.** FTIR spectra for sodium isocyanoureate with 100% HNO<sub>3</sub> (left) and  $H_2SO_4/HNO_3 = 85\%/15\%$  (right).

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