

Generation of Melamine Polymer Condensates upon Hypergolic Ignition of Dicyanamide Ionic Liquids**

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Fuels that can be ignited chemically under ambient conditions—upon contact with an oxidizing agent—are referred to as hypergols.^[1] Engines powered by hypergols do not require electric ignition, thus making them simple, robust, and reliable alternatives to conventional fossil fuels. Commonly used hypergolic fuels include hydrazine and its methylated derivatives, which are extremely toxic, corrosive, and have high vapor pressure. Intense research is underway to develop alternative environmentally friendly liquid propellants with lower toxicity to reduce operational costs and safety requirements associated with handling hydrazine.^[2] Ionic liquids (ILs)^[3] have recently received considerable attention as energetic materials for propellant applications owing to lower vapor pressures, higher densities and, often, an enhanced thermal stability compared to their nonionic analogues.^[4] Since 2008, a number of ILs have been reported to be hypergolic when treated with common oxidizers, such as HNO_3 .^[5–7] Of particular practical interest are hypergolic ILs comprising fuel-rich dicyanamide (DCA) anions.^[5] The DCA ILs have some of the lowest viscosities among known ILs,^[8] which is a very important figure of merit for the efficient fuel supply in bipropellant engines.

In this study, by using electrospray ionization mass spectrometry (ESI-MS), we discovered that the reaction between DCA ILs and HNO_3 yields a precipitate that is composed of cyclic triazines, including melamine and its polymers. The concurrent formation of precipitate siphons materials from the hypergolic reaction pathway,^[6] thus limit-

ing the energy capacity of a fuel. Our rough measurements indicate that about 25% of DCA IL is converted into precipitate during the ignition. Furthermore, the generation of stable solid-state species during the ignition indeed represents a serious problem for the safe operation of bipropellant engines. The results of model experiments obtained under various experimental conditions suggest that the key components necessary for the formation of the major polymers are DCA anions and nitric acid. Polymerization occurs even at lower concentration of reagents, when neither hypergolic ignition nor notable heating of the reaction mixture take place. The reaction of DCA ILs with aqueous HNO_3 therefore represents a new, facile, ambient method to synthesize cyclic azines, which can be tuned by choosing from a variety of different IL precursors.

The condensate was found to be poorly soluble in water as well as in a set of organic solvents, including dichloromethane, acetonitrile, chloroform, methanol, toluene, ethyl acetate, and diethyl ether. The solubility dramatically increased, however, in ammonium hydroxide (10% vol), thus suggesting the high content of nitrogen atoms in the species constituting the precipitate.

Figure 1 shows positive and negative ion mode mass spectra of the precipitate formed in the reaction between 1-butyl-3-methyl-imidazolium dicyanamide and white fuming HNO_3 (WFNA, ca. 100%) after dissolution in ammonium hydroxide. Note that all the peaks in Figure 1 were also observed from the liquid phase of the residue suspension in pure water without ammonia, although at a considerably lower intensity caused by its much decreased solubility. Consequently, we can exclude the possible origin of these peaks as a result of chemical reaction between the residue and ammonia.

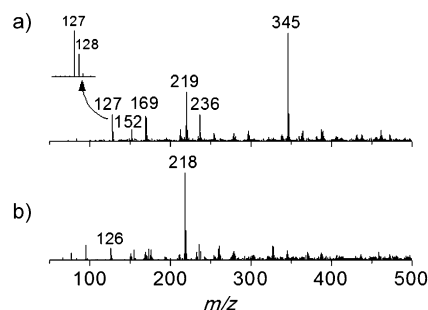


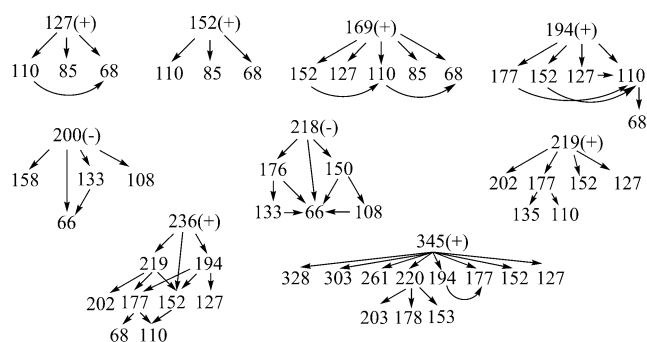
Figure 1. ESI-MS spectra of the precipitate formed during the reaction between 1-butyl-3-methylimidazolium dicyanamide and WFNA. The precipitate was dissolved in an aqueous solution of ammonia (10% vol) and analyzed directly in positive (a) and negative (b) ion detection modes.

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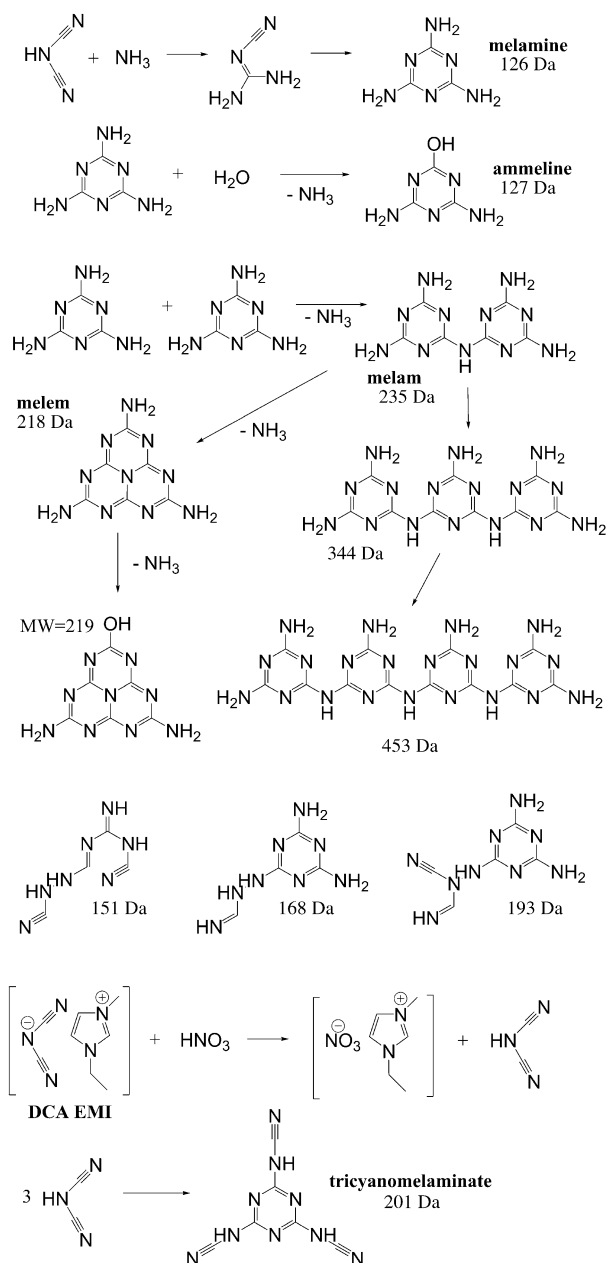
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Scheme 1. Tandem MS analysis of major species constituting the precipitate formed during the reaction of DCA ILs with HNO_3 (Figure 1 and Figure 2). Common fragmentation channels include multiple neutral losses of ammonia (17 Da), hydrogen cyanamide, NCNH_2 (42 Da), and hydrogen dicyanamide $\text{N}(\text{CN})_2\text{H}$ (67 Da).

Scheme 1 summarizes the results of tandem MS analysis for each peak. We observe common fragmentation channels, which correspond to multiple neutral losses of ammonia (17 Da), hydrogen cyanamide NCNH_2 (42 Da), and hydrogen dicyanamide $\text{N}(\text{CN})_2\text{H}$ (67 Da). The similarity of fragmentation channels suggests structural homology of the detected species. Based on the fragmentation patterns in Scheme 1, the peak at m/z 127 appears to be an essential structural building block for most of the compounds. From high-resolution MS analysis the only chemical formula associated with this peak was calculated to be $\text{C}_3\text{N}_6\text{H}_7^+$. We propose that the identity of this species is protonated melamine based on the reported tandem mass spectra for this compound that contain fragments at m/z 110, 85, and 68.^[9] We confirmed this assignment by a reference experiment on authentic melamine. Melamine is known to be produced from DCA through reaction with ammonia to yield cyanoguanidine,^[10] which then polymerizes into melamine,^[11] as shown in Scheme 2. Possible sources of ammonia in our experiments are discussed later in this Communication.

The peaks at m/z 127, 236, and 345 in Figure 1a are separated from each other by 109 mass units, thus indicating the polymerization of melamine (Scheme 2). The “dimer” is commonly referred to as melam (235 Da) and is known to be a product of thermal condensation of melamine.^[12] Upon heating, melam is known to lose ammonia to form melem (218 Da).^[13] Melem can also be generated by thermal treatment of other less-condensed C–N–H compounds, such as melamine, dicyandiamide, ammonium dicyanamide, or cyanamide.^[13,14] As follows from its fragmentation pattern (Scheme 1), the species at m/z 169 consists of melamine with cyanamide attached, and this species can be an intermediate during the polymerization of melamine to melam and melem (Scheme 2, 168 Da). The species at m/z 152 is formed from m/z 169 by the loss of ammonia (Scheme 1). It is probably the only species out of those detected in which the *s*-triazine ring structure is broken (Scheme 2, 151 Da). The peaks described above were detected for all the DCA ILs tested in this study (see the Experimental Section).



Scheme 2. Structures and mechanisms for the formation of the species observed in the reaction between dicyanamide ILs and nitric acid.

Most of the peaks in Figure 1a are accompanied by peaks with a shift of one mass unit. These adjacent peaks have the same nominal mass but much stronger relative intensities than those expected from ^{13}C isotopes (e.g. see the inset in Figure 1a for a doublet m/z 127–128). As derived from high-resolution mass spectrometry measurements, these peaks arise from the substitution of NH_2 functionality with OH. For example, the corresponding substituent for melamine is referred to as ammeline (Scheme 2, 127 Da) and is readily produced from melamine by hydrolysis in strong acid.^[15] The presence of the OH group was supported by the MS/MS analysis that revealed the neutral loss of 18 mass units (water). Upon hydrolysis of triazine functional groups to

hydroxyl groups, the latter become visible in negative ion detection mode by deprotonation of OH groups (Figure 1b). For example, the peak at m/z 126 corresponds to deprotonated ammeline and the peak at m/z 218 to hydroxy-substituted melem. The latter dominates the spectrum in negative ion mode probably because melem is most predisposed to hydrolysis to its hydroxy-substituted version.

Thermal decomposition into melamine-like cyclic azines has been reported for a number of energetic materials.^[16,17] For example, the formation of melamine, melem, melon, and ammeline has been observed from dicyandiamide, diaminoglyoxime, and diaminofurazan when heated at a rate of 100°C s^{-1} at a pressure of up to 1000 psi of Ar.^[16] The DCA ILs with nitrogen-containing cations have recently been reported to condensate into triazine rings at $\sim 500^\circ\text{C}$, and upon further heating (up to ca. 1000°C) gave rise to dense nitrogen-doped carbon materials.^[18]

To explore the factors responsible for the formation of precipitate during the reaction of DCA ILs with nitric acid, a set of experiments was performed in which various DCA ILs were mixed in bulk with aqueous HNO_3 (10 % vol). As a result of the lower concentration of components, the reaction was much slower and no ignition occurred. Still, we observed vigorous bubbling, thus indicating release of volatile products, and finally, after about 1 min, formation of a precipitate. Under these conditions, SEM images (see the Supporting Information) reveal that the precipitate has a larger particle size distribution as compared to the precipitate formed during hypergolic ignition. Solid- and liquid-phase products were isolated by centrifuging and then analyzed separately. The solution phase was diluted in water ($\times 10^{-3}$) and then analyzed using direct-infusion ESI-MS. Figure 2a shows the resulting mass spectrum in negative ion detection mode when the DCA

IL with the 1-ethyl-3-methylimidazolium (EMI) cation was used.

The spectrum is dominated by clusters with the molecular composition of $[\text{EMI}^+]_{n-1}[\text{NO}_3^-]_n$ ($n \geq 1$), thus pointing at the formation of $[\text{EMI}^+][\text{NO}_3^-]$ salt during the reaction. It can be concluded from this observation that HNO_3 and $[\text{EMI}^+][\text{DCA}^-]$ IL undergo ion exchange— EMI^+ pairs with NO_3^- to form water-soluble salt, while DCA^- interacts with protons to yield the precipitate (Scheme 2). The EMI^+ cations remain intact (Figure 2a), thus indicating that the temperature does not reach decomposition threshold during the reaction.^[19]

The precipitate was washed in water and then dissolved in ammonium hydroxide (10 % vol) for ESI-MS analysis. Analogous to the precipitate formed under the conditions of hypergolic ignition (Figure 1), the precipitate from the model reaction between DCA ILs and aqueous HNO_3 also reveals the presence of melamine and its oligomers (Figure 2b and c), including the one at m/z 454 (453 Da, Scheme 2). However, as follows from the mass spectrum, new polymerization channels arise: the peak at m/z 194 in positive ion mode and m/z 200 in negative. Based on tandem MS analysis (Scheme 1), the compound at m/z 194 was found to consist of dicyanamide attached to melamine (Scheme 2, 193 Da). This observation points possibly to a lower-energy polymerization pathway of melamine than that associated with the intermediate at m/z 169 observed under hypergolic conditions (Scheme 2, 168 Da). The peak at m/z 200 was identified as a dicyanamide trimer, known as tricyanomelaminat (Scheme 1 and Scheme 2). In our experiments, each tricyanomelaminat molecule originates from three DCA anions and three protons donated by nitric acid, and this is in full agreement with the ion exchange reaction mechanism proposed above. We suggest that the formation of tricyanomelaminat becomes a dominant polymerization channel at lower concentration of reagents because less ammonia is eliminated during the reaction, which decelerates the concurrent polymerization of DCA into melamine (Scheme 2).

The fact that the composition of precipitate does not depend on the IL cation suggests that the latter does not take part in the reaction. In agreement with this hypothesis, we found that sodium dicyanamide (Na DCA) produces the same azine species when reacted with aqueous HNO_3 under nitrogen atmosphere, including melamine, melam, melem, ammeline, and tricyanomelaminat. Therefore, it can be concluded that ammonia necessary for the synthesis of melamine polymers is formed during the reaction between DCA and HNO_3 ; possibly, it originates from the dinitrobiuret intermediate.^[6] The latter easily decomposes into HNCO ,^[20] which is then hydrolyzed to yield NH_3 and CO_2 .^[21] The reaction does not occur when HCl , CH_3COOH , or aqueous NaNO_3 are used instead of HNO_3 to oxidize Na DCA. It is also worth noting that while mere heating of Na DCA up to about 300°C does generate tricyanomelaminat,^[22] mixing Na DCA with aqueous HNO_3 (10 % vol) yields tricyanomelaminat as well as melamine and its oligomers without notable increase in temperature. These observations indicate that the formation of precipitate in our experiments cannot be attributed to heating or change in pH. The critical components to induce polymerization are DCA and nitrate anions as

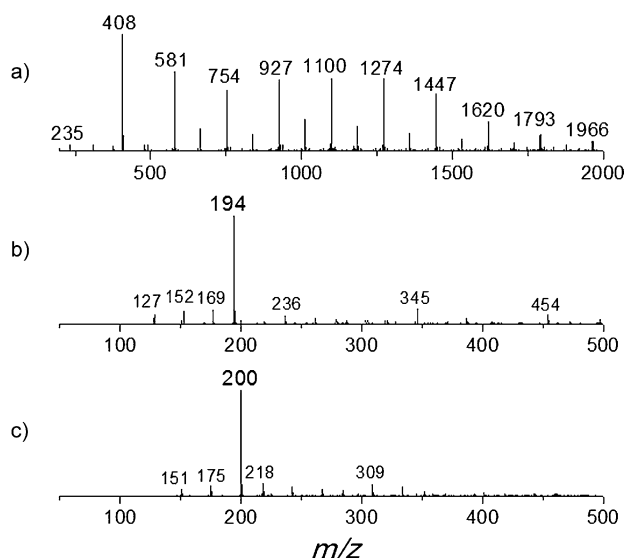


Figure 2. Products of the reaction between 1-ethyl-3-methylimidazolium dicyanamide and aqueous nitric acid (10 % vol) analyzed by ESI-MS: a) solution phase (diluted 10^3 times in pure water) analyzed in negative ion detection mode; b) and c) are the MS of the precipitate (dissolved in ammonium hydroxide) analyzed in positive and negative ion detection modes, respectively.

well as free protons (no reaction with NaNO_3 !), which are also key components in the proposed mechanism for the hypergolicity of DCA ILs.^[6]

In summary, we found that various *s*-triazine compounds are generated during the ignition of hypergolic dicyanamide ionic liquids with nitric acid, among which we identified melamine and its oligomers, for example, melam and melem. The formation of the major polymers through decomposition of DCA ILs is mediated by nitric acid and competes with the hypergolic oxidation mechanism. Although our discovery imposes certain implications on the use of DCA ILs as bipropellant fuels, it demonstrates an interesting approach to facile, ambient synthesis of cyclic azines, which constitute the forefront of modern carbon nitride chemistry.^[23] Condensation is readily achieved by mixing DCA IL with HNO_3 at ambient temperature and pressure. The concomitant ignition can be avoided during the synthesis simply by sufficient dilution of the oxidizer in water prior to reaction.

Experimental Section

Hypergolic reaction was initiated when a drop of WFNA introduced from a gastight syringe fell into a small cuvette containing a small amount (ca. 0.5 mL) of IL fuel. Liquid was decanted, and the residue was centrifuged and washed in water 30 times. The recovered precipitate was dissolved in ammonium hydroxide and then directly analyzed by ESI-MS in both positive and negative ion detection modes. Most MS and MS^n ($n \geq 2$) analyses were performed on a Finnigan LCQ Classic mass spectrometer (Thermo, San Jose, CA, USA). Because the efficiency of collision-induced dissociation in LCQ is limited by the need to trap fragment ions, for some low molecular weight species ($m/z < 200$) complementary MS^2 analysis was carried out using a quadrupole time-of-flight instrument (QTOF, Waters, Manchester, UK) to provide more abundant fragmentation. High-resolution mass spectrometry measurements were done on an Orbitrap Exactive mass spectrometer (Thermo, San Jose, CA, USA).^[24] DCA ILs with the following cations were purchased: 1-butyl-1-methyl-pyrrolidinium, *N*-butyl-3-methylpyridinium (EMD Chemicals Inc., Darmstadt, Germany), 1-ethyl-3-methylimidazolium, and 1-butyl-3-methyl-imidazolium (Fluka Analytical, Steinheim, Germany). Nitric acid was obtained from Fisher Scientific (Hampton, NH, USA) and melamine from Fluka.

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