

THERMAL STUDIES OF AMMONIUM CYANIDE REACTIONS: A MODEL FOR THERMAL ALTERATION OF PREBIOTIC COMPOUNDS IN METEORITE PARENT BODIES. P. G. Hammer¹, D. R. Locke², A. S. Burton³ and M. P. Callahan¹, ¹Boise State University, Department of Chemistry and Biochemistry, Boise, ID 83725, ²HX5 – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, ³Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX 77058. Email: michaelcallahan914@boisestate.edu

Introduction: Organic compounds in carbonaceous chondrites were likely transformed by a variety of parent body processes including thermal and aqueous processing. Here, we analyzed ammonium cyanide reactions that were heated at different temperatures and times by multiple analytical techniques. The goal of this study is to better understand the effect of hydrothermal alteration on cyanide chemistry, which is believed to be responsible for the abiotic synthesis of purine nucleobases and their structural analogs detected in carbonaceous chondrites [1].

Samples and Analytical Techniques: Ammonium cyanide (1.0 M) was prepared and transferred to a glass vial inside a Parr Instruments high-pressure reaction vessel. The vessel was evacuated using a vacuum pump and heated using an oil bath. Several solutions were heated at incremental temperatures (50, 100, 150, and 200 °C) for 3, 24, and 72 hours. In addition, room temperature samples (~20 °C) were prepared, transferred to an ampoule, flame sealed with minimal headspace, and allowed to react for >6 months. Resulting samples were centrifuged and decanted to remove cyanide (CN) polymer from supernatant. CN polymer was washed with nanopure water four times before drying in a vacuum centrifuge.

Both CN polymer and supernatant were analyzed using a Perkin Elmer Spectrum-100 FT-IR spectrometer equipped with a universal ATR sampling accessory (zinc selenide/diamond) and operated under triple bounce mode. 50 scans were acquired per sample with a 1 cm⁻¹ resolution. Samples of the polymer were sent to NASA Johnson Space Center for tetramethylammonium hydroxide (TMAH) thermochemolysis (250 and 500 °C in pyrolysis unit) and gas chromatography-mass spectrometry (GC-MS) analysis. Compound identification was accomplished through comparison of acquired electron ionization (EI) mass spectra to the NIST 14 mass spectral database. Supernatant was analyzed using a Thermo Scientific Accela high performance liquid chromatograph (HPLC) with photodiode array detector (200 - 400 nm) and compared to nitrogen heterocycle reference standards and their corresponding retention times.

Results and Discussion: We obtained FT-IR spectra of both the supernatant and polymer isolated from 1.0 M ammonium cyanide reactions heated at different

reaction temperatures and times. The FT-IR spectrum of our room temperature polymer sample closely resembled spectra of HCN polymer obtained by other research groups [2, which can also be referred to for some peak assignments]. As the reaction temperature increases from room temperature to 200 °C, there are noticeable changes that can be observed in the FT-IR spectra, particularly in the 1700-1000 cm⁻¹ range, which suggests structural alteration took place in *both* supernatant and polymer as temperature increased. To investigate these changes further at the molecular level, we used GC-MS and HPLC to analyze the polymer and supernatant, respectively.

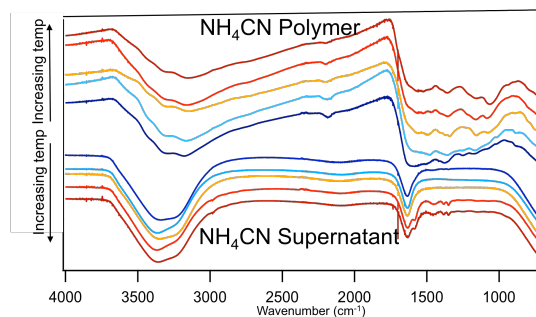


Figure 1: FT-IR spectra of CN polymer (top series) and supernatant (bottom series) isolated from 1.0 M ammonium cyanide reactions heated at different reaction temperatures.

Using TMAH-pyrolysis GC-MS, the polymer was studied through methylation of fragmented portions of the polymer. We analyzed polymers isolated from ammonium cyanide reactions heated to 50, 150, and 200 °C for 72 hours (as well as polymer isolated from a 6-month room temperature reaction) with this technique. The dominant products were methyl derivatives of urea and formamide (see Figure 2), which were detected in all four polymer samples. We also detected different classes of nitrogen heterocycles: pyrimidines (dihydrouracil), purines (adenine, guanine, xanthine, and hypoxanthine), and triazines (cyanuric acid), a suite of organics comparable to what Matthews and Minard detected using a similar analytical approach [3]. However, these nitrogen heterocycles appear only as minor products and seem to decrease as reaction

temperature increased. Although these data are qualitative, there is a general decrease in overall products with higher reaction temperature and an associated increase in aromatic compounds (e.g., benzene, phenanthrene). These results suggest that higher reaction temperatures produced some char (highly aromatic coal-like structure) with the CN polymer.

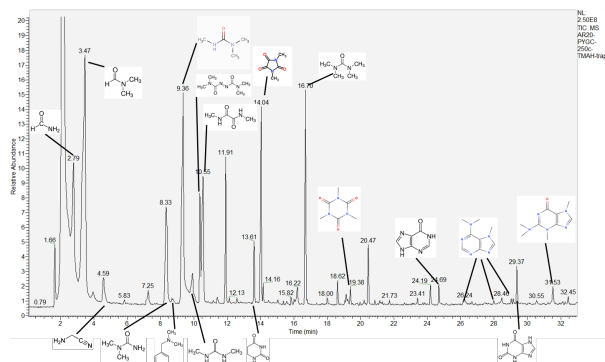


Figure 2: GC-MS chromatogram acquired after TMAH thermochemolysis (250 °C) of the CN polymer generated from 1.0 M ammonium cyanide (room temperature, >6 months).

We analyzed the unhydrolyzed supernatant from ammonium cyanide reactions that were heated to different temperatures by HPLC with UV detection. The temperature series for 72 hours is shown in Figure 3. Many peaks were observed in these UV chromatograms, which suggested that complex molecules (aromatics and/or heterocycles) were still present throughout the entire temperature series. We specifically screened these samples for purines and pyrimidines that were previously known in concentrated ammonium cyanide reactions [1,4]. We tentatively identified adenine in the supernatant portion for the entire temperature series. Previously, Borquez et al. reported adenine yields from the (unhydrolyzed) supernatant of 0.1 M ammonium cyanide as a function of temperature (-78, -20, 60, 80, and 100 °C). They showed that adenine yields were only slightly greater at higher temperatures, which suggested that adenine yield is not strongly dependent on temperature [5]. We also tentatively identified guanine, hypoxanthine, and 6,8-diaminopurine, which are all purines. We did not detect cytosine above our detection limit (10 pmol) in any of our supernatants; however, a peak that correlates to thymine was measured in the lower temperature ammonium cyanide reactions (20 and 50 °C). HPLC-UV is helpful for preliminary analyses of these samples; however, ultimate confirmation of structure will be made from liquid chromatography-mass spectrometry analyses.

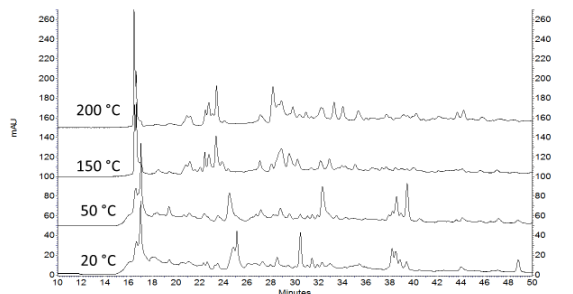


Figure 3: HPLC chromatograms (at 260 nm) of the supernatant of 1.0 M ammonium cyanide heated at various temperatures for 72 hours.

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References: [1] Callahan M. P. et al. (2011) *PNAS*, 108, 13995–13998. [2] de la Fuente J. L. et al. (2014) *Polym. Degrad. Stab.*, 110, 241–251. [3] Matthews C. N. and Minard R. D. (2006) *Faraday Discuss.*, 133, 393–401. [4] Miyakawa S. et al. (2002) *Orig. Life Evol. Biosph.*, 32, 209–218. [5] Borquez E. et al. (2005) *Orig. Life Evol. Biosph.*, 35, 79–90.