

**ABIOLICAL NITROGEN: FORMATION OF NITROGENATED ORGANIC AEROSOLS IN THE TITAN UPPER ATMOSPHERE.** H. Imanaka<sup>1,2,3</sup> and M. A. Smith<sup>1,2</sup>, <sup>1</sup>Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ (himanaka@email.arizona.edu), <sup>2</sup>Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, <sup>3</sup>SETI Institute, Mountain View, CA.

**Introduction:** Nitrogen is an essential biotic element, yet difficult to fix into biotic/prebiotic molecules directly from N<sub>2</sub>. Despite N<sub>2</sub> being the most abundant constituent in the Earth atmosphere through most of its history, only limited fixed nitrogen is available for the biosphere. In the thick N<sub>2</sub> atmosphere of Titan with a trace amount of methane, atmospheric chemistry leads eventually to heavy organic gaseous species and aerosol particles. Understanding the formation chemistry and the resulting chemical structure of possible nitrogenated organic aerosols in the Titan atmosphere might help in constraining the atmospheric contribution in abiotic nitrogen fixation processes relevant to the origin and evolution of early life.

Many aspects of the nitrogen fixation process by EUV-VUV photochemistry in the Titan atmosphere are not fully understood. The recent Cassini mission revealed organic aerosol formation in the upper atmosphere of Titan [1]. Although the nitrogeous compounds are definitely suggested as trace amounts [2], bulk nitrogen fixation in Titan's atmosphere is not well constrained at present. It has been generally believed that the CN unit originated from the ground state N(<sup>4</sup>S) atom plays a central role in Titan's nitrogen chemistry [3,4]. However, a substantial amount of the excited N(<sup>2</sup>D) atom is also generated from N<sub>2</sub> photodissociation and photoionization. Recently, crossed molecular beams studies of the N(<sup>2</sup>D) reactions with CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> reveal the products of CH<sub>2</sub>NH isomers, C<sub>2</sub>H<sub>3</sub>N isomers, and HCCN, respectively [5-7]. These highly reactive species might be important precursors for the nitrogenated complex molecules and organic aerosols. We have succeeded to generate photolytic aerosol samples from a N<sub>2</sub>/CH<sub>4</sub> gas mixture at wavelengths sufficient for dissociation and ionization of N<sub>2</sub>, demonstrating the important role of N(<sup>2</sup>D) in the nitrogenated organic aerosol formation.

**Experimental:** Our experiments are conducted using a synchrotron radiation source (Chemical Dynamics Endstation, 9.0.2) at the Advanced Light Source (ALS) [8,9]. A gas mixture of N<sub>2</sub>/CH<sub>4</sub> (=95/5) flows through the windowless photocell chamber during continuous irradiation of EUV-VUV photons separately at 60 nm and 82.5 nm. The neutral gas species are analyzed *in situ* using a quadrupole mass spectrometer (QMS) with electron impact ionization. The solid sample is accumulated on a copper plate as a thin film, whose optical thickness growth is monitored with UV-

Visible reflectance interferometric spectroscopy. The solid samples are kept under vacuum and subsequently analyzed with a Laser Desorption/Ionization-Fourier Transform Ion Cyclotron Resonance-Mass Spectrometry (LDI-FTICR-MS).

**QMS analysis of neutral gaseous species:** The obtained neutral mass spectra naturally show the complex overlaps from isobaric compounds and fragmentation ions. One direct way to constrain the upper limit of nitrogenous products is to compare the obtained mass spectra of nitrogen/methane irradiation from separately <sup>13</sup>C and <sup>15</sup>N isotope labeled initial gas mixtures. The shift toward heavier mass with <sup>13</sup>C labeling clearly indicates the incorporation of carbon from the initial gas mixture (Fig. 1a). In contrast, the comparison of the mass spectra from gas mixtures of <sup>14</sup>N<sub>2</sub>/CH<sub>4</sub> and <sup>15</sup>N<sub>2</sub>/CH<sub>4</sub> irradiated at 60 nm shows no obvious shift in the observed MS spectra (Fig. 1b). The upper limit of the contribution of nitrogenated species to the spectral intensity is 10 % for the m/z range larger than 50 ((C+N)<sub>4</sub> and above).

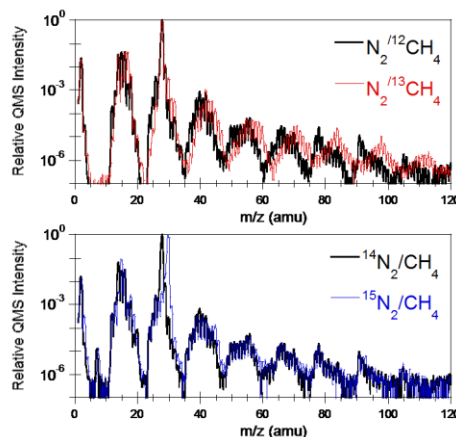


Figure 1. QMS analysis of gaseous products from 60nm irradiation of the isotope substituted nitrogen/methane (=95/5) gas mixtures. The QMS intensities are normalized for N<sub>2</sub> peak intensities. (a) Comparison of N<sub>2</sub>/<sup>12</sup>CH<sub>4</sub> and N<sub>2</sub>/<sup>13</sup>CH<sub>4</sub>. (b) Comparison of <sup>14</sup>N<sub>2</sub>/CH<sub>4</sub> and <sup>15</sup>N<sub>2</sub>/CH<sub>4</sub>.

**LDI-FTICR-MS analysis of organic aerosol samples.** The LDI-FTICR-MS analyses of the accumulated aerosol samples at 60 nm and 82.5 nm irradiation (here after, UV\_600 and UV\_825 samples) reveal more than 5000 peaks between 200 – 700 m/z in the mass spectra. This ultra-high mass resolution analysis

( $M/\Delta M = 3 \times 10^7$ ) enables the unambiguous assignments of CHNO formulae of several thousand molecules in the mass range. Unlike the gaseous sample, most of the observed ions from the solid contain nitrogen, and only a few pure hydrocarbon ions are observed in these samples. The bulk C/N ratios in the UV\_600 and UV\_825 are estimated to be  $1.6 \pm 0.3$  and  $1.1 \pm 0.2$ , respectively.

In order to investigate the functional diversity and the possible precursors, all identified ion species are plotted with the aid of van Krevelen diagrams (Fig. 2). This perspective clearly reveals the distinct nitrogen incorporation in organic macromolecules at 60 nm and 82.5 nm irradiation. Most species at 82.5 nm irradiation are distributed around  $H/C = 1$  and  $N/C = 1$ , implying HCN as the important precursor. On the other hand, the distribution in the UV\_600 is more carbon-rich with only a few peaks around  $H/C = 1$  and  $N/C = 1$ , indicative of HCN not being the major seed at 60 nm. Although the UV\_600 sample shows a wide diversity in constituents, the integration of MS intensity in the van Krevelen diagram (Fig. 2b) suggests the dominant chemical constituents are the congeners with the bulk ratio of  $C_2H_2N$ . Considering the previous experiment demonstrating that hydrogenation is much faster than H-abstraction for H-atom heterogeneous reactions of this type of material [10], the HCCN radical is most likely, but not exclusively, the dominant precursor at 60 nm irradiation.

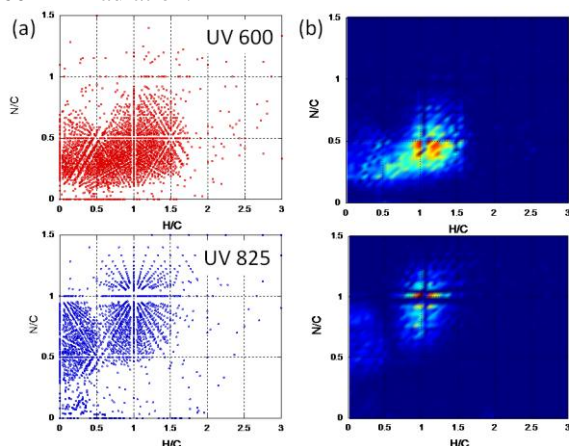


Figure 2. Ultra-high-mass-resolution LDI-FTICR-MS analyses of photolytically generated organic aerosols at 60 nm (UV\_600) and 82.5 nm (UV\_825) irradiation of a  $N_2/CH_4$  ( $= 95/5$ ) gas mixture. (a) Van Krevelen diagrams ( $N/C$  vs  $H/C$ ) of all identified  $C_xH_yN_z^+$  compounds. (b) Cumulative MS intensities shown as van Krevelen diagrams.

**HCCN radical as an important precursor for nitrogenated organic solid production.** The efficient formation of unsaturated hydrocarbons is observed in

the gas phase without abundant nitrogenated neutrals at 60 nm, while the solid components are dominated with heavily nitrogenated species. This strongly suggests a direct nitrogen incorporation mechanism of short lived nitrogenated reactive species into solid products via heterogeneous chemistry. The ultrahigh-mass-resolution study of  $N_2/CH_4$  photolytic solid products at 60 nm and 82.5 nm define the distinct nitrogen incorporations, suggesting important roles of  $H_2C_2N/HCCN$  and  $HCN/CN$  in their respective formation. However, the much slower production rate of the UV\_825 sample over that of the UV\_600 suggests that nitrogen incorporation into organic aerosols proceeds via  $N(^2D)$  and HCCN, more efficiently than via  $N(^4S)$  and  $HCN/CN$  pathways, and our experiments cast doubt on the popular HCN/CN based neutral/radical mechanism of nitrogenated organic aerosol production in Titan's atmosphere.

**Implication for Titan's atmosphere:** In the upper atmosphere of Titan, the presence of both  $N(^2D)$  atom and unsaturated hydrocarbons most likely leads to the formation of HCCN,  $C_2H_3N$ , and  $CH_2NH$ . Under the the dusty environment in Titan's thermosphere and mesosphere [1,11], the heterogeneous reaction of HCCN radicals is the plausible nitrogen incorporation mechanism for aerosol growth (Fig 3). The dissociated nitrogen in the form of excited N atoms is efficiently removed by incorporation into solid aerosols rather than observed as stable gaseous species. Therefore, organic aerosols in the upper atmosphere of Titan might be a hidden N sink, which eventually accumulate on the surface of Titan with chemical potential for prebiotic evolution.

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