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Laboratory investigations of Titan haze formation: In situ measurement of gas and particle composition

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ABSTRACT

Prior to the arrival of the Cassini-Huygens spacecraft, aerosol production in Titan's atmosphere was believed to begin in the stratosphere where chemical processes are predominantly initiated by far ultraviolet (FUV) radiation. However, measurements taken by the Cassini Ultraviolet Imaging Spectrograph (UVIS) and Cassini Plasma Spectrometer (CAPS) indicate that haze formation initiates in the thermosphere where there is a greater flux of extreme ultraviolet (EUV) photons and energetic particles available to initiate chemical reactions, including the destruction of N_2. The discovery of previously unpredicted nitrogen species in measurements of Titan's atmosphere by the Cassini Ion and Neutral Mass Spectrometer (INMS) indicates that nitrogen participates in the chemistry to a much greater extent than was appreciated before Cassini. The degree of nitrogen incorporation in the haze particles is important for understanding the diversity of molecules that may be present in Titan's atmosphere and on its surface. We have conducted a series of Titan atmosphere simulation experiments using either spark discharge (Tesla coil) or FUV photons (deuterium lamp) to initiate chemistry in CH_4/N_2 gas mixtures ranging from 0.01% CH_4/99.99% N_2 to 10% CH_4/90% N_2. We obtained *in situ* real-time measurements using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) to measure the particle composition as a function of particle size and a proton-transfer ion-trap mass spectrometer (PIT-MS) to measure the composition of gas phase products. These two techniques allow us to investigate the effect of energy source and initial CH_4 concentration on the degree of nitrogen incorporation in both the gas and solid phase products. The results presented here confirm that FUV photons produce not only solid phase nitrogen bearing products but also gas phase nitrogen species. We find that in both the gas and solid phase, nitrogen is found in nitriles rather than amines and that both the gas phase and solid phase products are composed primarily of molecules with a low degree of aromaticity. The UV experiments reproduce the absolute abundances measured in Titan's stratosphere for a number of gas phase species including C_4H_2, C_6H_6, HCN, CH_3CN, HC_3N, and C_2H_5CN.

1. Introduction

The discovery of very heavy ions (negative ions with mass-to-charge up to 10,000 amu/q (Coates et al., 2007), positive ions with mass-to-charge up to 400 amu/q (Crary et al., 2009)) in Titan's thermosphere has dramatically altered our understanding of the processes involved in the formation of the complex organic aerosols that comprise Titan's characteristic haze. Prior to the arrival of the Cassini-Huygens spacecraft, aerosol production was believed to begin in the stratosphere where chemical processes are predominantly initiated by far ultraviolet (FUV) radiation. However, the discovery of very heavy ions, coupled with Cassini Ultraviolet Imaging Spectrograph (UVIS) occultation measurements that show haze absorption up to 1000 km (Liang et al., 2007), indicates that haze formation initiates in the thermosphere. The energy environment of the thermosphere is significantly different from the stratosphere; in particular there is a greater flux of extreme ultraviolet (EUV) photons and energetic particles available to initiate chemi-

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cal reactions, including the destruction of N_2, in the upper atmosphere. The discovery of previously unpredicted nitrogen species in measurements of Titan's atmosphere by the Cassini Ion and Neutral Mass Spectrometer (INMS) indicates that nitrogen participates in the chemistry to a much greater extent than was appreciated before Cassini (Vuitton et al., 2007). Additionally, measurements obtained by the Aerosol Collector Pyrolyzer (ACP) carried by Huygens to Titan's surface may indicate that Titan's aerosols contain significant amounts of nitrogen (Israël et al., 2005; 2006). Additionally, Sebree et al. (2014) recently showed that the inclusion of nitrogen bearing aromatic precursors in laboratory atmosphere simulation experiments results in particles that are a better fit to the far IR spectrum of Titan aerosols obtained from Cassini CIRS. Previous Titan atmosphere simulation experiments have also demonstrated that the presence of nitrogen increases the complexity of both the gas and aerosol phase chemistry (Fujii and Arai, 1999; Imanaka and Smith, 2007; 2009; Trainer et al., 2012) and may play a key role in increasing the efficiency of gas to particle conversion (Trainer et al., 2012). The degree of nitrogen incorporation in the haze particles is important for understanding the diversity of molecules that may be present in Titan's atmosphere and on its surface. The building blocks of life as we know it, such as amino acids and nucleotide bases, require the presence of nitrogen and previous Titan atmosphere simulation experiments have demonstrated that gas phase and/or heterogeneous chemistry results in the formation of some of these building blocks including molecules such as adenine ($C_5N_5H_5$) (Hörst et al., 2012).

For nearly 50 years, mixtures of N_2 and CH_4 have been subjected to a variety of energy sources in numerous different experimental setups to produce Titan aerosol analogues, so-called "tholins", and investigate both the gas and solid phase products. These energy sources include protons, laser induced plasma (LIP), gamma rays, corona discharge, electrical discharge, UV lamps (Hg or deuterium), and UV synchrotron. Recent comprehensive reviews of Titan atmosphere simulation experiments, including a detailed discussion of various energy sources, can be found in Cable et al. (2012) and Coll et al. (2013). It can be very difficult to compare the results of simulation experiments from different laboratories because of the differences in experimental setup (temperature, pressure, gas mixture, and energy source) and analysis techniques. Our unique experimental setup allows for direct comparison between the products formed by two different energy sources, spark discharge and UV, without any other differences in experimental technique, materials, or analysis techniques. This allows for investigation of the effect of energy source on the incorporation of nitrogen into tholin without any other variables.

We have conducted a series of Titan atmosphere simulation experiments using either spark discharge (Tesla coil) or FUV photons (deuterium lamp) to initiate chemistry in CH_4/N_2 gas mixtures ranging from 0.01% CH_4/99.99% N_2 to 10% CH_4/90% N_2. We have obtained *in situ* measurements using three different techniques. We use a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) to measure the particle composition as a function of particle size, a proton-transfer ion-trap mass spectrometer (PIT-MS) to measure the composition of gas phase products, and a scanning mobility particle sizer (SMPS) to measure particle size distributions. These three techniques allow us to investigate the effect of energy source and initial CH_4 concentration on the degree of nitrogen incorporation in both the gas and solid phase products, the size and number of particles, and particle density. The size and density measurements from these experiments have been published in Hörst and Tolbert (2013) and will be discussed here only as they relate to interpretation of the other measurements.

2. Materials and experimental methods

2.1. Haze production setup

A schematic of the experimental setup is shown in Fig. 1. Previous spark experiments were performed using a similar setup by Trainer et al. (2004a, 2004b) and Hörst and Tolbert (2013) and previous UV experiments were performed by Trainer et al. (2006, 2012, 2013) and Hörst and Tolbert (2013). Reactant gases, N_2

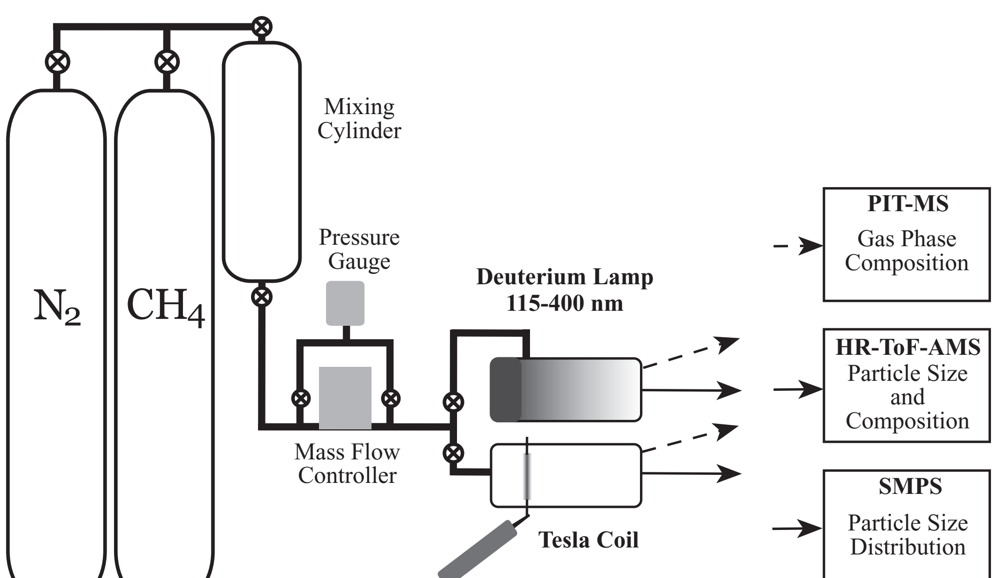

Fig. 1. Schematic of the experimental setup used for this work. N_2 and CH_4 are mixed overnight in the mixing cylinder. Gases flow through one of two reaction cells (UV or spark) where they are exposed to FUV photons from a deuterium lamp or the electric discharge produced by a Tesla coil initiating chemical processes that lead to the formation of new gas phase products and particles. The composition of the gas phase products is then measured using a proton-transfer ion-trap mass spectrometer (PIT-MS). The particles are analyzed using either a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) to measure their composition or a scanning mobility particle sizer (SMPS) to measure their size distribution. Each reaction cell has two outlets; the dashed lines indicate where teflon lines, fittings, and valves were used while the solid lines indicate stainless steel lines, fittings, and valves. All experiments were run at room temperature and 620–640 Torr (atmospheric pressure in Boulder, Colorado).