Icarus 289 (2017) 214–226

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

The Titan Haze Simulation (THS) experiment on COSmIC. Part II. Ex-situ analysis of aerosols produced at low temperature

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ARTICLE INFO

Article history:
Received 9 August 2016
Revised 10 December 2016
Accepted 9 February 2017
Available online 21 February 2017

Keywords:
Aeronomy
Atmospheres, Chemistry
Experimental techniques
Spectroscopy
Titan, Atmosphere

ABSTRACT

This paper presents the first results of the solid phase analysis of the Titan tholins generated in the Titan Haze Simulation (THS) experiments. This study complements the gas phase analysis study that was presented in a previous publication introducing the THS capabilities. In the THS experiment, the chemistry is simulated by plasma in the stream of a supersonic jet expansion. With this unique design, the gas is jet-cooled to Titan-like temperature (~150 K) before inducing the chemistry by plasma, and remains at low temperature in the plasma discharge (~200 K).

Here, we present and discuss the results of scanning electron microscopy and infrared spectroscopy studies of THS solid aerosols produced in the four gas mixtures already studied by mass spectrometry in the gas phase: N_2–CH_4, N_2–CH_4–C_2H_2, N_2–CH_4–C_6H_6 and N_2–CH_4–C_2H_2–C_6H_6. Differences in the morphology of the grains and aggregates produced in the volume of the gas phase in the plasma cavity, depending on the initial precursors, have been observed by scanning electron microscopy, that appear to be linked to differences in the growth processes and might have an impact on microphysical models. The mid-infrared spectroscopic analysis highlights changes in the nitrogen chemistry, and the abundance of aromatic compounds, depending on the initial gas mixture. A preliminary study of the aging and degradation of the THS samples with time and exposure to air and light has shown the importance, for future studies of laboratory-generated planetary aerosol analogs, of collecting, storing and characterizing samples under controlled environment. A comparison to VIMS data shows that the THS tholins produced in simpler mixtures, i.e., with a higher level of nitrogen incorporation, are more representative of Titan's aerosols.

1. Introduction

Ever since the Voyager 1 mission revealed the presence of organic molecules and haze in Titan's dense nitrogen-based atmosphere (Kunde et al., 1981; Maguire et al., 1981), the largest satellite of Saturn has been subjected to a close scrutiny. Numerous laboratory and modeling studies have been conducted to attempt to decipher the chemistry between N_2 (95–98%) and CH_4 (5–2%) that leads to the formation of complex organic molecules and solid aerosols (Cable et al., 2011; Raulin et al., 2012; Müller-Wodarg et al., 2014, and references therein). Especially since 2004, when the instruments of the Cassini/Huygens mission started returning unexpected observational data that unraveled a much more complex system than expected. In particular, the presence of ion-neutral chemistry in the upper atmosphere, and of heavy positively and negatively charged molecules and particles was unanticipated (Cravens et al., 2006; Coates et al., 2007; Waite et al., 2007; Crary et al., 2009). A combination of observational data analysis, theoretical and experimental studies is the key to unraveling the complex chemistry in Titan's atmosphere.

The ambient conditions in Titan's atmosphere make the laboratory experiments difficult to implement. The pressure is high, 1.5 bar, at the surface, but much lower in the regions of the atmosphere where chemistry is expected to occur and initiate the formation of solid aerosols (around 10^{-6}–10^{-7} mbar at 1000–1200 km), as well as in the regions where the distinctive haze layers are formed (around 10^{-1}–10^{-2} mbar at 250–400 km altitude) (Fulchignoni et al., 2005). The temperature varies from 94 K at the surface to as low as 70 K at the tropopause and as high as 180 K in the upper atmosphere (Fulchignoni et al., 2005). The ideal laboratory experiment would therefore require simulating Titan's atmospheric chemistry at low pressure and low temperature. How-

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http://dx.doi.org/10.1016/j.icarus.2017.02.004
0019-1035/

ever, realistically, the pressure achieved in the laboratory cannot be as low as on Titan if one wants to observe detectable chemistry in the laboratory time scale (weeks to months at most). The frequency of collisions at that low a pressure would be so small that it would take too long to induce a chemical reaction let alone generate products in large enough quantity to be detected by laboratory instruments. It is therefore necessary to use higher pressures in laboratory experiments to accelerate the chemical processes and produce detectable heavier species and solid aerosols in a realistic time frame. The low temperature is not impossible to achieve but not an easy task either, which is why most laboratory experiments are done at room temperature (see reviews in Cable et al., 2011, Raulin et al., 2012 and references therein). Another challenge for laboratory experiments is finding the proper energy source to induce the chemistry. Cable et al. (2011), and references therein) described in details the different energy sources (plasma discharges, UV irradiation, gamma radiation and soft X-rays, proton and electron beams) that have been used in Titan simulation experiments. The most common two types of energy sources are UV irradiation and plasma discharges. Both present advantages and disadvantages. As already discussed in our previous publication (Sciamma-O'Brien et al. 2014), the main advantage of using a plasma discharge in Titan laboratory experiments as opposed to UV lamp irradiation comes from the capability of the former to dissociate nitrogen, hence simulating electron bombardment due to Titan's interaction with Saturn's magnetosphere. On Titan, the extreme UV solar photons and electrons present in Saturn's magnetosphere have high enough energies to dissociate nitrogen ($>$ 9.76 eV, $<$ 127 nm), therefore permitting chemical pathways that are not simulated in laboratory photolysis experiments, which are usually performed in the far-UV (FUV) range (115–200 nm – the dissociation cross section of N_2 above 115 nm is extremely low, making it highly improbable to dissociate nitrogen). Even though incorporation of nitrogen in tholins produced by photolysis of N_2–CH_4 has been observed in FUV lamp experiments, it is thought to be due, in part, to the occurrence of tri-molecular reactions (Trainer et al., 2013) and does not represent the nitrogen chemistry induced by the dissociation of nitrogen on Titan. Several synchrotron experiments have been performed with high-energy beams capable of dissociating nitrogen (Imanaka and Smith 2007, 2010; Thissen et al., 2009) but they usually use a narrow bandwidth, not representative of the solar energy distribution. A new reactor installed on the SOLEIL synchrotron allows for a simulation over a wider wavelength range from 60 to 350 nm, but so far only gas phase analyses have been published (Peng et al., 2013). In plasma experiments, the electron energy distribution function (EEDF) is closer in shape to the broad solar spectrum energy distribution, producing electrons with a wide range of energies, including a tail of higher energy electrons that can dissociate nitrogen, allowing for chemical pathways that involve the presence of nitrogen atoms. This has been demonstrated in Szopa et al. (2006) where they compared two Maxwell-Boltzmann EEDF calculated for electron temperatures of 1 and 2 eV (representative of the THS experiment – Remy et al., 2003a,b) to the solar spectrum distribution. It is important to note, though, that continuous plasmas can over-process the chemical products and the resulting aerosols (Carrasco et al., 2016).

The Titan Haze Simulation (THS) experiment developed at NASA Ames Research Center on the COsmic SImulation Chamber (COSmIC), uses a cold pulsed plasma discharge as the energy source to induce the chemistry. The features that make the THS different from other plasma experiments are: (1) the use of a supersonic jet expansion that cools down the initial gas mixture to temperatures representative of Titan's chemistry (∼150 K) *before* inducing the chemistry by plasma discharge; (2) the use of a *pulsed* plasma discharge in the stream of the expansion (i.e., an accelerated gas with short residence time in the plasma discharge) that results in a truncated chemistry and prevents the over processing of the chemical products and resulting aerosols; and (3) the possibility to incrementally add heavier precursors in the initial gas mixture to probe the intermediary steps and isolate specific pathways in the chemical reaction chain. In a recently published study of the gas phase chemistry using time-of-flight mass spectrometry, we demonstrated the potential of the THS to study the different steps of Titan's atmospheric chemistry at low temperature (Sciamma-O'Brien et al., 2014, hereafter called Part I). We studied four different gas mixtures with increasing precursor complexity: N_2–CH_4-based gas mixtures with two hydrocarbon precursors, acetylene (C_2H_2) and benzene (C_6H_6), to investigate some specific pathways associated with the presence of these trace constituents in Titan's atmosphere.

Here we present the results of a complementary study of the solid phase using similar gas mixtures that allow probing the different steps of the aerosol formation. In the THS experiment, solid particles, grains and aggregates are produced in volume in the gas phase, within the plasma cavity, and can be deposited onto different substrates for further ex situ analyses. In this study, two ex situ diagnostics have been used to characterize the aerosols produced in the THS: scanning electron microscopy (SEM) to study the morphology of the grains, and infrared spectroscopy to derive information on the functional groups present in the aerosols and study the effects of acetylene and benzene on the final aerosol composition. We have compared our laboratory data to observational data from the Cassini VIMS instrument as well as other Titan tholin IR studies, to illustrate the potential of the THS experiment to help interpret the observational data and reach a better understanding of Titan's atmospheric chemistry. In the following sections, we first describe the experimental setup and present the different ex situ analyses performed on the THS aerosols, before discussing the results.

2. Experimental setup

2.1. COSmIC simulation chamber: cold plasma in jet-cooled expansion

The THS experiment has been described in detail in Part I (Sciamma-O'Brien et al., 2014, and references therein). Here, we give a brief summary of the experimental setup and how it operates, with a focus on the solid phase production and collection. In the THS, a pulsed plasma discharge is used as the energy source to induce chemistry and form Titan aerosol analogs from various gas mixtures. A pulsed discharge nozzle (PDN) mounted on a vacuum chamber is employed to produce a planar plasma jet expansion, as shown in Fig. 1. A gas mixture is injected into a copper reservoir and escapes in 1.28 ms-long pulses through a 4.6 mm-thick plate with a 100 mm x 127 µm-thin slit ((a) in Fig. 1), thereby producing a planar supersonic jet expansion. The gas pressure and temperature drop adiabatically. The pulsed gas then expands at Mach 1 into a plasma cavity formed by a 1.5 mm-thick alumina dielectric plate with a 100 mm x 400 µm slit ((b) in Fig. 1), and the gas pressure and temperature drop to 30 mbar and 150 K, respectively (Biennier et al., 2006; Benidar, 2012; Contreras and Salama, 2013). Within the 1.28 ms gas pulse, a pulsed (10 Hz) negative voltage (from −600 V (6.0 mA) to −1000 V (9.9 mA)) is applied onto a set of Elkonite (90% tungsten, 10% copper) cathodes mounted 400 µm apart along the slit on the alumina plate, in order to generate a 300 µs-long pulsed plasma discharge in the jet-cooled gas. The cold plasma produced within the cavity (between anode and cathodes) induces the chemistry between the different constituents of the injected gas mixture. The pressure in the plasma cavity is higher (30 mbar) than in the regions of Titan's atmosphere where complex gas species and haze have been detected. This higher pressure is necessary in order to enhance the chemistry for the chemical re-