



Identification of nitrogenous organic species in Titan aerosols analogs: Nitrogen fixation routes in early atmospheres



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ARTICLE INFO

Article history:

Received 21 March 2013

Revised 25 April 2013

Accepted 17 May 2013

Available online 28 May 2013

Keywords:

Titan

Atmosphere

Organic chemistry

Prebiotic chemistry

ABSTRACT

Titan, an icy world surrounded by auburn organic haze, is considered as one of the best targets for studying abiotic planetary organic chemistry. In spite of a great many efforts being made, the chemistry in Titan's atmosphere and its resulting chemical structures are still not fully understood. In our previous work, we have investigated the structure of Titan aerosols analogs (tholin) by NMR and identified hexamethylenetetramine as a dominant small molecule in Titan tholin. Here we report a more complete and definitive structural investigation of the small molecule inventory in Titan tholin. We identified several nitrogenous organic molecules including cyanamide, guanidine, 2-cyanoguanidine, melamine, N'-cyanoformamidine and 1,2,4-triazole in Titan tholin by using NMR and GC-MS and standard sample comparison. The structural characteristics of these molecules suggest a possible formation pathway from the reaction of HCN and NH₃, both of which are known to exist in appreciable density in the atmosphere and were tentatively detected by the Huygens probe.

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1. Introduction

Titan is the largest moon of the Saturnian system and also the only moon having a significant atmosphere in the Solar System, an icy world surrounded by reddish brown organic haze. The recent Cassini–Huygens mission revealed a great deal of information about Titan and deepened our knowledge of this moon immensely. Complex organic chemistry takes place in Titan's thick atmosphere and generates a multitude of simple organic molecules, leading to complex organic aerosols and condensate layers in the atmosphere (see e.g. Sagan et al., 1992; Flasar et al., 2005; Niemann et al., 2005, 2010). The aerosols analogs (tholin) were found to contain a significant percentage of nitrogen-rich organic molecules and hydrocarbons (Sagan et al., 1993; Coll et al., 1999, 2013; Imanaka et al., 2004; Cable et al., 2012). These molecules could exist in Titan's aerosols, which fall to the surface of Titan and may react with periodic liquid water (O'Brien et al., 2005; Neish et al., 2006; Lorenz et al., 2008) to yield prebiotic species (Khare et al., 1984, 1986; Neish et al., 2010; Horst et al., 2012). Titan is similar to primitive Earth in some ways, such as its dense, nitrogen-rich atmosphere, liquid surface and energy sources (Sagan et al., 1992; Clarke and Ferris, 1997; Raulin, 2007; Hayes et al., 2011). The general

ingredients involved in the processes of chemical evolution and prebiotic chemistry are organic matter, liquid water, and energy, which are all present on Titan. Thus, Titan is considered as a prebiotic laboratory at the planetary scale and one of the best objects for studying developing young planetary organic chemistry.

However, the chemistry and the resulting chemical structures are still not clear. This is especially true for the nitrogenous organic molecules which are detected as significant components in Titan's atmosphere (Vuitton et al., 2007), but are not well constrained regarding how the nitrogen atoms are fixed directly from N₂. To understand the chemical processes and the structures of possible nitrogenated organic aerosols in Titan's atmosphere, Titan aerosols analogs (tholin) have been prepared in the laboratory by electrical discharges or photochemical reactions in nitrogen–methane mixture (Cable et al., 2012; Coll et al., 2013). Laboratory simulations and analysis provide critical insight to Titan's organic chemistry. Much structural information of the tholin materials has been obtained from laboratory analysis, such as UV/Vis spectroscopy (Imanaka et al., 2004), IR spectroscopy (Sagan et al., 1993; Coll et al., 2001; Imanaka et al., 2004; Ramirez et al., 2004; Quirico et al., 2008; Ruiz-Bermejo et al., 2008, 2009; Gautier et al., 2012), UV/Vis fluorescence (Hodyss et al., 2004), pyrolysis–chromatography (McGuigan et al., 2006), elemental analysis (McKay, 1996) and mass spectrometry (Coll et al., 1999; Sarker et al., 2003; Hodyss et al., 2004; McGuigan et al., 2006; Somogyi et al., 2005, 2012; Imanaka and Smith, 2007, 2009, 2010; Pillig

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et al., 2009; Ruiz-Bermejo et al., 2009; Thissen et al., 2009; Neish et al., 2009, 2010; Pernot et al., 2010; Horst et al., 2012) as well as NMR spectroscopy (Sagan et al., 1993; Clarke et al., 2000; Ramirez et al., 2004; Ruiz-Bermejo et al., 2008, 2009; He et al., 2012a, 2012b; Derenne et al., 2012). However, acquiring the definitive organic structures within the complex mixture is a challenging task.

In our previous study, we have reported the initial structural analysis of tholin samples using 1D NMR techniques (He et al., 2012a). The obtainable information from the simple spectral analysis and coupling study provides a small molecule functional inventory and polymer chemical environment conclusion (He et al., 2012a). We also identified the most concentrated component in the Titan tholin, which is hexamethylenetetramine (HMT) by combining multinuclear and multidimensional NMR spectroscopy. One of its precursor, 1,3,5-hexahydrotriazine, was also detected (He et al., 2012b). In the present paper, we report the identification of more nitrogenous organic species in Titan tholin by using NMR spectroscopy and Gas chromatography–mass spectrometry (GC–MS), including cyanamide, guanidine, 2-cyanoguanidine, melamine, N'-cyanoformamidine and 1,2,4-triazole. The structural characteristics of these molecules suggest an important chemical pathway via HCN and NH₃ for nitrogenous organic aerosol formation in nitrogen/methane rich planetary atmospheres.

2. Experimental

2.1. Production of tholin

The ¹³C and ¹⁵N isotopic labeled tholin samples were prepared by exposing a mixture of 5% ¹³CH₄ (¹³C 99.9%, Cambridge Isotope Laboratories) and 95% ¹⁵N₂ (¹⁵N 98%+, Cambridge Isotope Laboratories) to a high frequency electrical discharge in a high vacuum stainless steel/glass reaction chamber at 195 K. The flow rate is set such that the pressure of the chamber is held at 850 Pa. The detailed procedure was described previously (He et al., 2012a, 2012b). The reaction vessel is allowed to warm to room temperature during a 24 h period under vacuum to remove the highly volatile lower molecular fraction. The polymeric solids were isolated in a dry, oxygen-free glove-box, and the samples were stored under N₂ atmosphere. Natural abundance tholin samples were prepared from a gas mixture of 5% CH₄ and 95% N₂ under the same condition.

2.2. Solution-state NMR spectroscopy

Approximately 20 mg of labeled tholin sample was dissolved into DMSO-*d*₆ (D 99.9%, anhydrous, Sigma–Aldrich). After 10 min, the sample was dissolved completely. The operation was carried out in a glove box under anaerobic and anhydrous conditions at room temperature. The samples were kept in sealed NMR tubes and wrapped in foil to avoid exposure to air and light, respectively. The solution-state NMR experiments were carried out on a Varian INOVA 600 spectrometer which is equipped with an H, C, N triple-resonance cryogenic probe with z-gradient. The experiments include multinuclear and multidimensional NMR experiments, such as 1D ¹H, ¹³C and ¹⁵N NMR experiments with different decoupling methods, two-dimensional (2D) ¹H–¹³C Heteronuclear Single Quantum Correlation (HSQC), ¹H–¹⁵N HSQC, ¹H–¹H Correlation Spectroscopy (COSY), ¹H–¹³C 2D correlation spectrum with ¹⁵N-filtering triple-resonance pulse sequence [¹H → ¹⁵N → ¹³C(*t*₁) → ¹⁵N → ¹H(*t*₂)] and ¹H–¹⁵N 2D correlation spectrum with ¹³C-filtering triple-resonance pulse sequence [¹H → ¹⁵N(*t*₁) → ¹³C → ¹⁵N → ¹H(*t*₂)].

For comparison, the solution-state 1D ¹H and ¹³C (even ¹⁵N for 2-cyanoguanidine) NMR spectra of standard natural abundance samples in DMSO-*d*₆ were acquired. The standard samples include

2-cyanoguanidine (99%, C₂H₄N₄), guanidine hydrochloride (≥99%, CH₅N₃–HCl), cyanamide (99%, CH₂N₂), melamine (99%, C₃H₆N₆) and 1,2,4-triazole (98%, C₂H₃N₃), which are all purchased from Sigma–Aldrich and used without further purification. 1D ¹H and ¹³C NMR spectra and 2D ¹H–¹³C HSQC spectrum of natural abundance tholin samples were also obtained. The ¹H and ¹³C chemical shifts (δ values) are referenced to tetramethylsilane (TMS), and ¹⁵N is referenced to NH₃.

2.3. Gas chromatography–mass spectrometry (GC–MS)

Natural abundance tholin samples were put into methanol and approx 70% of the solid samples were soluble. The solutions were analyzed on a GC–MS spectrometer (Trace Mass, Thermo Fisher Scientific Inc.), which is equipped with an Rtx-5MS column. A 1 μL sample was injected into the GC injector at a splitting ratio of 1:30 and analyzed using both the full scan (29–300) and SIM mode. The MS is a quadrupole mass spectrometer and the ionization energy is 70 eV. The temperatures at the inlet, MS transfer line and ion source were set at 280 °C, 250 °C and 250 °C, respectively. The carrier gas was He (99.999%) with constant flow (1.5 mL/min). The temperature program for the column was set at an initial temperature of 120 °C for 1 min, a rate of temperature increase of 20 °C/min and final temperature of 300 °C for 3 min. The standard sample methanol solutions (2-cyanoguanidine, cyanamide and melamine) were also analyzed on the GC–MS spectrometer using the same parameters.

3. Results and discussions

In this article, we describe the identification of several nitrogenous organic species in Titan tholin by using NMR spectroscopy and Gas chromatography–mass spectrometry (GC–MS).

3.1. NMR results and identification of 2-cyanoguanidine

Fig. 1 is the ¹H spectrum of ¹³C and ¹⁵N labeled Titan tholin, in which the strongest peak (9.5% of the proton spectrum) at 4.54 ppm has been assigned to HMT (He et al., 2012b). Another strong peak at 6.58 ppm is a little broader and the integration result shows that it accounts for approx 7% of the total proton spectrum, indicating another major component in tholin. Since this spectrum is not ¹³C or ¹⁵N decoupled, all the peaks are doublets caused by ¹³C–¹H or ¹⁵N–¹H one-bond coupling. The peak at 6.58 ppm is an obvious doublet and the coupling constant is 89.7 Hz which is a typical ¹⁵N–¹H one-bond coupling (Breitmaier

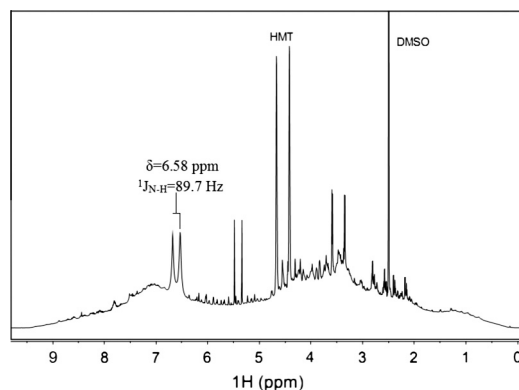


Fig. 1. ¹H spectrum of ¹³C and ¹⁵N labeled Titan tholin without ¹³C and ¹⁵N decoupling.

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