

A comprehensive NMR structural study of Titan aerosol analogs: Implications for Titan's atmospheric chemistry



Chao He*, Mark A. Smith

Department of Chemistry, University of Houston, Houston, TX 77204, United States

ARTICLE INFO

Article history:

Received 27 May 2014

Revised 9 September 2014

Accepted 11 September 2014

Available online 19 September 2014

Keywords:

Titan, atmosphere
Organic chemistry
Prebiotic chemistry

ABSTRACT

Titan has a thick atmosphere composed primarily of nitrogen and methane. Complex organic chemistry induced by solar ultraviolet radiation and energetic particles, takes place in Titan's upper atmosphere, producing an optically thick reddish brown carbon based haze encircling this moon. The chemistry in Titan's atmosphere and its resulting chemical structures are still not fully understood in spite of a great many efforts being made. In our previous work, we have investigated the structure of the ^{13}C and ^{15}N labeled, simulated Titan haze aerosols (tholin) by NMR and identified several dominant small molecules in the tholin. Here we report our expanded structural investigation of the bulk of the tholin by more comprehensive NMR study. The NMR results show that the tholin materials are dominated by heavily nitrogenated compounds, in which the macromolecular structures are highly branched polymeric or oligomeric compounds terminated in methyl, amine, and nitrile groups. The structural characteristic suggest that the tholin materials are formed via different copolymerization or incorporation mechanisms of small precursors, such as HCN , $\text{CH}_2=\text{NH}$, NH_3 and C_2H_2 . This study helps to understand the formation process of nitrogenated organic aerosols in Titan's atmosphere and their prebiotic implications.

© 2014 Elsevier Inc. All rights reserved.

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 extensive information about Titan and deepened our knowledge of this moon immensely. Complex organic chemistry takes place in the thick atmosphere of Titan and generates thousands of organic molecules, leading to organic aerosols and condensate layers in the atmosphere (Sagan et al., 1992, 1993; Coll et al., 1999, 2013; Cable et al., 2012). The aerosols are believed to contain a significant percentage of nitrogen-rich organic molecules and hydrocarbons (Coll et al., 2013; Imanaka et al., 2004; Cable et al., 2012), which fall to the surface 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). Titan is similar to primitive Earth in both basic physical properties and energy sources, and the chemistry occurring on Titan might be similar to that which occurred on the young Earth. Thus, Titan is considered

as a prebiotic laboratory on the planetary scale and one of the best objects for studying planetary organic chemistry. However, beyond the simplest of molecules, the chemistry and the resulting chemical structures present are still not clear. Without detailed structural identification of mid-sized molecules ($\text{C} > 4$), our mechanistic knowledge of the chemical processes on Titan truncates at the simplest level.

Tholins, Titan aerosol analogs, have been prepared in the laboratory by electrical discharges or photochemical reactions in nitrogen–methane mixture (Coll et al., 2013; Cable et al., 2012), to simulate the chemical processes believed to be active in the Titan haze production. Various methods, including 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; Pilling 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

* Corresponding author. Present address: Department of Earth and Planetary Science, Johns Hopkins University, 3400 N. Charles Street, Olin Hall 128, Baltimore, MD 21218, United States.

E-mail address: che4@central.uh.edu (C. He).

et al., 2012; He and Smith, 2013, 2014a, 2014b), has been applied to determine the unique properties of different tholins. Much useful information of the tholin materials has been obtained by these studies. However, definitive structural identification within the complex mixture was rarely reported, until our recent study employing multinuclear and multidimensional NMR spectroscopy (He et al., 2012a, 2012b; He and Smith, 2013, 2014b). We have obtained a general small molecule structural inventory and polymer chemical environment conclusion from simple 1D NMR spectral analysis and coupling study (He et al., 2012a) and identified several nitrogenous organic molecules in the Titan tholin (He et al., 2012b; He and Smith, 2013, 2014b), including cyanamide (CH_2N_2), 2-cyanoguanidine ($\text{C}_2\text{H}_4\text{N}_4$), melamine ($\text{C}_3\text{H}_6\text{N}_6$), guanidine hydrocyanide ($\text{C}_2\text{H}_6\text{N}_4$), N'-cyanofornamide ($\text{C}_2\text{H}_3\text{N}_3$), 1,2,4-triazole ($\text{C}_2\text{H}_3\text{N}_3$), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), 1,3,5-hexahydrotriazine ($\text{C}_3\text{H}_9\text{N}_3$), succinonitrile ($\text{C}_4\text{H}_4\text{N}_2$), aminoacetonitrile ($\text{C}_2\text{H}_4\text{N}_2$), adenine ($\text{C}_5\text{H}_5\text{N}_5$) and acetoguanamine ($\text{C}_4\text{H}_7\text{N}_5$), whose structures are shown as a to l in Fig. 1. The ^1H signals of these molecules are labeled in the ^1H spectrum of Titan tholin in d_6 -DMSO and their ^1H percentages of total protons in the tholin from the integration of the quantitative ^1H spectrum are shown on the right (Fig. 1). The protons in the identified molecules account for 8.5% of total protons in the tholin. 91.5% of protons in the tholin are still not identified and most of them are represented by unresolved broad peaks contributed by polymers. In the present paper, we continue the structural investigation of the tholin by advanced NMR techniques and obtain a more comprehensive understanding of the bulk of the tholin. The structural information suggests possible chemical pathways for nitrogenated organic aerosols in Titan, involving copolymerizations or incorporations of small precursors, such as HCN, $\text{CH}_2=\text{NH}$, NH_3 and C_2H_2 .

2. Experimental

2.1. Production of tholin

The ^{13}C and ^{15}N isotopically labeled tholin samples were prepared by exposing a mixture of 5% $^{13}\text{CH}_4$ (^{13}C 99.9 atom%, Cambridge Isotope Laboratories) and 95% $^{15}\text{N}_2$ (^{15}N 98+ atom%, Cambridge Isotope Laboratories) to a high frequency electrical discharge in a high vacuum stainless steel/glass reaction chamber at 195 K. The detailed procedure has been 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 weight fraction and inhibit further chemistry in the condensate. The polymeric solids were isolated in a dry, oxygen-free glove-box, and the samples were stored under N_2 atmosphere.

2.2. Solution-state NMR spectroscopy

Approximately 20 mg of the solid sample was dissolved into fresh d_6 -DMSO (D 99.9 atom%, 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 equipped with an H, C, N triple-resonance cryogenic probe with z-gradient. The proton-related multidimensional NMR experiments were performed, including 1D ^1H , and 1D $^{13}\text{C}/^{15}\text{N}$ -filtered ^1H spectra, 2D ^1H - ^{13}C Heteronuclear Single Quantum Correlation (HSQC), ^1H - ^{15}N HSQC, ^1H - ^{13}C and ^1H - ^{15}N Edited-HSQC, ^1H - ^1H Correlation Spectroscopy (COSY), ^1H - ^{15}N correlation spectrum acquired with ^{13}C -filtering triple-resonance pulse sequence [$^1\text{H} \rightarrow ^{13}\text{C} \rightarrow ^{15}\text{N}(t_1) \rightarrow ^{13}\text{C} \rightarrow ^1\text{H}(t_2)$] and ^1H - ^{13}C correlation spectrum acquired with ^{15}N -filtering triple-resonance pulse sequence [$^1\text{H} \rightarrow ^{15}\text{N} \rightarrow ^{13}\text{C}(t_1) \rightarrow ^{15}\text{N} \rightarrow ^1\text{H}(t_2)$] (Sattler et al., 1999; Lambert and Mazzola, 2004). The ^1H , ^{13}C and ^{15}N chemical shifts are referenced to TMS, TMS and NH_3 , respectively.

3. Result and discussion

3.1. $^{13}\text{C}/^{15}\text{N}$ -filtered ^1H spectra of Titan tholin

Fig. 2 shows the ^1H NMR spectra of Titan tholin. The sample is ^{13}C and ^{15}N labeled and the ^1H spectra are acquired without decoupling, so all protons are coupled to bonded ^{13}C and ^{15}N and the peaks are primary doublets. These spectra clearly indicate the sharp peak at 4.42/4.67 ppm is from the proton bonded to ^{13}C and the peak at 5.34/5.49 ppm is from the proton bonded to ^{15}N . Taking these two peaks as reference, integration of all the peaks in Fig. 2b and c determines the ratio of the protons bonded to ^{13}C to the protons bonded to ^{15}N , which is approx 4:3. In addition, most peaks in Fig. 2b are distributed from 0 to 5 ppm while most peaks in Fig. 2c are above 5 ppm, suggesting that most of the protons bonded to carbon are connecting to saturated carbons

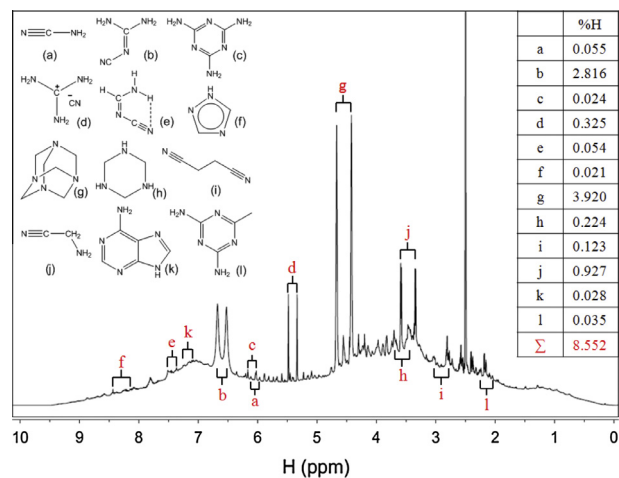


Fig. 1. ^1H spectrum of Titan tholin in d_6 -DMSO with identified small molecules labeled, a–l, whose structures are shown on the left and ^1H percentages are shown on the right.

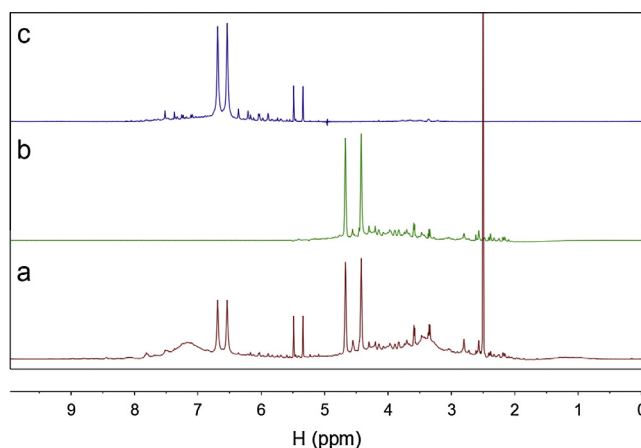


Fig. 2. ^1H NMR spectra of Titan tholin in d_6 -DMSO: (a) standard ^1H spectrum without decoupling, (b) ^{13}C -filtered ^1H spectrum, and (c) ^{15}N -filtered ^1H spectrum. The peak at 2.5 ppm in (a) is from the proton impurity in DMSO. (b) Only exhibits the protons bonded to ^{13}C , while (c) only exhibits the protons bound to ^{15}N .

Download English Version:

<https://daneshyari.com/en/article/1773080>

Download Persian Version:

<https://daneshyari.com/article/1773080>

[Daneshyari.com](https://daneshyari.com)