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Thermal degradation of organics for pyrolysis in space: Titan's atmospheric aerosol case study

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ABSTRACT

Pyrolysis coupled with mass spectry is among the instrumentation the most implemented in planetary exploration probes to analyze the chemical composition of extraterrestrial solid samples. It is used to analyze the volatile species which can be thermally extracted from the samples, including the organic fraction which is of primary interest for astrobiological purposes. However the thermal degradation of these organic materials, which can be very complex in nature or very different from organics commonly present on Earth, is badly known. This leads to a restriction in the optimization of space instrumentation, and in the interpretation of the measurements. In the present work we propose a complete overview of the thermal degradation processes studied on a model of complex organic material produced in an extraterrestrial environment, *i.e.* laboratory analogues of Titan's atmospheric aerosols. The thermal evolution of the studied analogues is monitored by following their mass loss, the emitted heating flux, and the evolution of their chemical composition through infrared spectroscopy and elemental analysis. The gaseous products released from the material are also analyzed by mass spectrometry, allowing to better constrain the mechanisms of chemical evolution of the samples. The complex organic material analyzed is found not to be fully decomposed when heated up to about 800 °C, with the evidence that nitrogen is still deeply incorporated in the remaining graphitic carbon nitride residue. The most appropriate pyrolysis temperature to chemically probe the studied material is found to be about 450 °C because at this temperature are detected the largest gaseous molecules which should be the most representative ones of the material pyrolyzed.

1. Introduction

Pyrolysis is the basic method used in space instrumentation for *in situ* characterization of the molecular composition of solid samples: Gas Chromatography–Mass Spectrometer and Sample Analysis at Mars instruments, respectively onboard the Viking and Curiosity probes, for Mars soil and rock samples (Biemann et al., 1977; Mahaffy et al., 2012), and very soon COmetary SAmpling and Composition instrument onboard the Rosetta probe for cometary surface materials (Goesmann et al., 2006). All the pyrolyzers used for space exploration are based on the oven pyrolysis principle whereas flash pyrolyzers (using Curie Point filament for example) are more commonly used in the laboratory (e.g. Coll et al., 2013). In all cases, the sample is automatically collected and transferred to the oven where it is heated to temperatures reaching from 500 °C (Viking GCMS experiment) to about 1000 °C (Curiosity SAM experiment). The gaseous species released from the samples are then transferred to the analytical part, generally using a chemically neutral gas (helium for the SAM and COSAC experiments) which continuously flows the oven during the pyrolysis. With such a sample preparation the SAM experiment helped to reveal the presence of oxychlorine in martian sand collected in Gale crater on Mars (Glavin et al., 2013; Leshin et al., 2013).

Pyrolysis has also been used as the preparative method for the *in situ* molecular analysis of Titan's aerosols, with the Aerosol Collector and Pyrolyzer coupled with the Gas Chromatography–Mass Spectrometry experiments, onboard the Huygens probe (Ehrenfreund et al., 1995; Israel et al., 2002). Titan's aerosols are indeed key components of Titan, as they drive many physical and chemical processes occurring in the atmosphere (Brown et al., 2009) or even at the surface of the biggest satellite of Saturn (e.g. Lorenz et al., 2006). The characterization of their physical and chemical properties is a primary goal to enhance our knowledge about this amazing world. The ACP and GCMS experiments have

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proven the presence of a solid organic part in the Titan's aerosols (Israel et al., 2005) that bears nitrogen atoms in a significant amount. This was determined thanks to the detection of HCN and NH_3 released when the aerosols have been heated up to 600 °C. But even if this was the first direct chemical analysis of Titan's aerosols, the interpretation of the results is limited because of the absence of detection of additional compounds, and by our ignorance of the aerosols building molecules.

Titan's aerosols cannot be directly characterized without using *in situ* measurements from an exploration probe. But potential chemical and physical properties of Titan's aerosols can be inferred from the study of analogues of aerosols produced in laboratory, also called "tholins". These studies are also very useful to help for the interpretation of remote sensing data (see Gautier et al., 2012; Sebree et al., 2014 for example). But in spite of numerous studies done up today with complementary analytical techniques (Cable et al., 2012), the chemical composition of tholins is still not well constrained. Moreover, among the analytical tools used for such studies, pyrolysis is particularly rarely implemented. Recently, Coll et al. (2013) used pyrolysis-gas chromatography–mass spectrometry (Pyr-GC–MS) to analyze different analogues provided by several teams around the world, and then compared the results to those obtained with the ACP experiment. They determined that the ACP results were better reproduced when pyrolyzing analogues of Titan's aerosols produced with "cold plasmas" techniques. This study was an important step for determining the best analogues to be used for mimicking pyrolysis of Titan's aerosols in the laboratory.

Nevertheless, the harsh pyrolysis done at 600 °C in the previous study does not give information about the pyrolysis process itself. This, prevents any inference about the initial aerosol structure and its progressive evolution with the temperature increase. This is the reason why the aim of this study is to address systematically the thermal degradation of Titan's aerosols analogues, using tholins produced with a "cold plasma" experiment (Szopa et al., 2006; Alcouffe et al., 2010). This laboratory work aims to better characterize the pyrolysis process of organic solid samples collected and analyzed in planetary environments, to better interpret the results that can be obtained in space. It is different, and somehow complementary, from a similar studies done by Nna-Mvondo et al. (2013) who investigated the difference of nature of Titan's tholins produced with different experimental set-ups, using thermal degradation.

2. Material and methods

2.1. Samples

For this work, the tholins sample was produced in the cold plasma experiment described in Szopa et al. (2006) and Alcouffe et al. (2010). A N_2/CH_4 (0.95:0.05) gaseous mixture flowed through the reactor at a 55 sccm total flow rate, and at room temperature. In these conditions the reactor pressure stabilizes at 1 mbar total pressure. The power absorbed by the plasma was set to 30 ± 2 W. After the experiment, the reactor was open to the laboratory atmosphere, and the solid organic powder formed from the gases in the dusty plasma was collected in inert vials, and then submitted to different types of analysis.

2.2. Thermal analysis

A systematic thermal degradation study of tholins has been carried out using the Thermal Gravimetry Analysis–Differential Scanning Calorimetry (TGA–DSC). Among the thermal analysis techniques, Thermal Gravimetry Analysis (TGA) is commonly used for characterizing the thermal properties of both inorganic and organic materials. It allows to measure the sample mass loss as a function of the sample temperature. The Derivative Thermal Gravimetry (DTG) can be used to investigate clearly the differences between thermograms, by enhancing the variation of the mass loss rate during the analysis. A Thermal Gravimetry Analyzer–Mass Spectrometer (TGA–MS) system was also used to analyze the main species released from the sample during its dynamic thermal decomposition.

TGA–DSC analyses were performed using a SENSYS evo (Setaram) TGA–DSC instrument, using a CALISTO software for data recording and treatment. The samples were placed in a 100 μL platinum crucible. The average sample mass put in the crucible was approximately 20 mg for each analysis. The samples were heated from the ambient temperature to 300 °C, 400 °C, 500 °C and 800 °C respectively at a 10 °C/min heating rate and in an argon (chemically inert) atmosphere to prevent any reactivity of the sample with the carrier gas. Once the maximum temperature (300 °C, 400 °C, 500 °C and 800 °C) was reached, the samples were kept for 1 h at the final pyrolysis temperature.

TGA–MS measurements were done by heating the sample with the TGA. During its heating, the sample releases gaseous volatile materials. These gases were analyzed by sampling on-line to a quadrupole mass spectrometer (QMS, Pfeiffer Balzers, OmniStar), equipped with Channeltron and Faraday detectors. The QMS m/z range is 2–300, but it was used in the 2–100 range for this study, to identify the main gaseous species released by the sample. It was used under the same conditions as for the TGA–DSC experiment.

2.3. Analysis of the heated residues

Infrared spectroscopy and elemental analysis were used to follow the chemical evolution of the solid material collected after the tholins heating, named "residue" in this study.

Infrared spectroscopy was performed using a Perkin–Elmer Spectrum One FTIR Spectrometer. Measurements were done in the 600–4000 cm^{-1} wavenumber range in this study. Each spectrum was obtained by addition of 4 scans with a 4.0 cm^{-1} spectral resolution of.

Elemental composition analyses of the tholins and the thermal residues were achieved with a FLASH 2000 Serie CHNS/Oxygen Automatic Elemental Analyzer instrument. C, H, N, and O mass percentages were measured in the initial tholins as well as in the thermal residues obtained at the different pyrolysis temperatures to study their composition variation. C, N and H were measured by flash combustion under a helium flow. The sample (1–2 mg) is weighed in Tin capsules (a capsule of silver for O analysis). It is placed inside the Thermo Scientific MAS200R auto sampler at a preset time, and then dropped into an oxidation or reduction reactor kept at a 900–1000 °C temperature. The exact amount of O required for the optimum combustion of the sample is delivered into the combustion reactor at a precise time. The gases released from this reaction, *i.e.* CO_2, H_2O and N_2, are separated and detected with a gas chromatograph. Oxygen determination is achieved with the same instrument but with an O specific pyrolysis reactor also flown with helium. The CO emitted by the specific reaction is then also analyzed using gas chromatography.

3. Results

The repeatability of the measurements has been first verified by performing four thermogravimetric measurements of the same material, under the same analytical conditions (see Fig. 1).