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Titan's organic aerosols: Molecular composition and structure of laboratory analogues inferred from pyrolysis gas chromatography mass spectrometry analysis

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ABSTRACT

Analogues of Titan's aerosols are of primary interest in the understanding of Titan's atmospheric chemistry and climate, and in the development of in situ instrumentation for future space missions. Numerous studies have been carried out to characterize laboratory analogues of Titan aerosols (tholins), but their molecular composition and structure are still poorly known. If pyrolysis gas chromatography mass spectrometry (pyr-GCMS) has been used for years to give clues about their chemical composition, highly disparate results were obtained with this technique. They can be attributed to the variety of analytical conditions used for pyr-GCMS analyses, and/or to differences in the nature of the analogues analyzed, that were produced with different laboratory set-ups under various operating conditions.

In order to have a better description of Titan's tholin's molecular composition by pyr-GCMS, we carried out a systematic study with two major objectives: (i) exploring the pyr-GCMS analytical parameters to find the optimal ones for the detection of a wide range of chemical products allowing a characterization of the tholins composition as comprehensive as possible, and (ii) highlighting the role of the CH_4 ratio in the gaseous reactive medium on the tholin's molecular structure. We used a radio-frequency plasma discharge to synthetize tholins with different concentrations of CH_4 diluted in N_2. The samples were pyrolyzed at temperatures covering the 200–700°C range. The extracted gases were then analyzed by GCMS for their molecular identification.

The optimal pyrolysis temperature for characterizing the molecular composition of our tholins by GCMS analysis is found to be 600°C. This temperature choice results from the best compromise between the number of compounds released, the quality of the signal and the appearance of pyrolysis artifacts. About a hundred molecules are identified as pyrolysates. A common major chromatographic pattern appears clearly for all the samples even if the number of released compounds can significantly differ. The hydrocarbon chain content increases in tholins when the CH_4 ratio increases. A semi-quantitative study of the nitriles (most abundant chemical family in our chromatograms) released during the pyrolysis shows the existence of a correlation between the amount of a nitrile released and its molecular mass, similarly to the previous quantification of nitriles in the plasma gas-phase. Moreover, numerous nitriles are present both in tholins and in the gas phase, confirming their suspected role in the gas phase as precursors of the solid organic particles.

1. Introduction

Titan's surface is well known for being hidden by a thick photochemical haze made of organic aerosols. Knowledge of the aerosol's chemical composition is of major importance since they play a prominent role in the radiative equilibrium of the satellite (Flasar et al., 2005; McKay et al., 1991). They contribute to the surface spectral signature (Tomasko et al., 2005), act as a sink for carbon-containing molecules in the gas phase (Lebonnois, 2002) and probably as condensation nuclei for the formation of clouds (Mayo and Samuelson, 2005). Moreover, Titan is the only body in the Solar System – besides Earth – to have a well-established

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complex organic chemistry. This particularity makes Titan one of the most interesting objects for astrobiology and the search for an extraterrestrial form of prebiotic chemistry in the Solar System (Raulin, 2007).

The chemical composition of Titan's organic aerosols remains poorly characterized in spite of the numerous results from the Cassini–Huygens space mission. The Cassini/VIMS and Cassini/CIRS infrared spectrometers did not provide detailed data on the aerosol composition (Hirtzig et al., 2013; Vinatier et al., 2012), neither did the Huygens/DISR experiment which analyzed the surface and atmosphere during the Huygens probe descent in 2005 (Tomasko et al., 2005). The Huygens/ACP-GCMS experiment analyzed the chemical composition of aerosols collected in the atmosphere. The condensed molecules present in the samples were released during a first heating at 250°C and analyzed by gas chromatography–mass spectrometry. The same procedure was done at 600°C to characterize the products of pyrolysis of the refractory core. Technical issues encountered by the ACP experiment were reported in the supplementary information of the Israel et al. (2005) article. They involved a leak of the sealing valve of the oven. The lack of tightness during the analysis prevented the efficient transfer of the volatile molecules released at 250°C to the GCMS experiment, resulting in the absence of an obvious GCMS signature of these molecules. These ACP issues however did not affect the MS analysis of the remaining refractory part of the sample extracted at 600°C. The experiment detected hydrogen cyanide (HCN) and ammonia (NH_3) in the 600°C pyrolysis products, proving that the aerosols are made up of a core of refractory organics – including N-bearing compounds – without any other information about the aerosol's molecular structure (Israel et al., 2002, 2005). Laboratory experiments are thus, to date, more likely to provide information about physical and chemical properties of the aerosols. This is the reason why Titan's aerosol laboratory analogues, named "tholins" in the following, have been studied since the 1980s (Khare et al., 1981).

Pyrolysis-GC–MS is one of the most commonly used techniques for the molecular analysis of tholins, because of its efficiency and simplicity of implementation. However the variability in the nature of the analogues (Cable et al., 2012), as well as in the conditions, instruments and techniques used for the analyses, leads to disparate results which are difficult to compare. Table 1 lists the analytical and sample synthesis conditions for all the previous pyr-GCMS studies. It shows that at least one parameter changes from one study to another, preventing definitive comparisons. For example, the choice of the chromatographic column impacts the type of compounds that can be analyzed. For instance, the use of a porous layer open tubular (PLOT) column generally focuses on volatile compounds (C_1 to C_5), whereas wall coated open tubular (WCOT) columns rather allow the separation of heavier compounds.

The most recent tholins analyses dismiss the hypotheses of a purely polymeric (poly-HCN, poly-HC_3N) or co-oligomeric (HCN–C_2H_2 or HCN–HC_3N) structure (Israel et al., 2002, 2005; Khare et al., 1981), in favor of a more irregular structure (Coll et al., 2013). Studies carried out with *a priori* comparable samples – synthetized from equivalent gas mixtures (N_2:CH_4, ratio 90:10) with cold plasma discharges – still diverge about the nature of the macromolecules. They are mostly aromatic or poly-aromatic hydrocarbons according to the Pyr-GCMS analysis by Coll et al. (1998). The study by McGuigan et al. (2006) reveals N-heterocycles (pyrroles) by GC×GC-TOF-MS analysis. And the nature of the macromolecules is found to be an open-chain structure according to the TG-MS study by Nna-Mvondo et al. (2013), who, on the contrary, do not detect any aromatic, polyaromatic or cyclic compound.

The compounds detected in previous studies of thermal degradation of tholins are listed in Table 2. All these molecules, produced from tholins pyrolysis, are divided into seven main chemical families: alkanes, alkenes, alkynes, aliphatic nitriles, aromatic nitriles, aromatic and cyclic hydrocarbons, and nitrogenous heterocycles. The "isomer" section of the table gives the empirical formula of the compounds whose exact isomeric structure could not be determined.

We should also mention that – except in the case of the study done by (Khare et al., 1981), where water was used in the initial gaseous mixture – the presence of oxygen bearing molecules, listed in the last section of the table, is due to a contamination, most probably by the molecular oxygen from the ambient air (Brassé, 2014).

As reported in Table 1, thermal degradation studies have been carried out on tholins produced under various experimental conditions. One of the main parameters is the composition of the initial gas mixture used for the synthesis (only CH_4 and N_2, or in presence of H_2O or H_2), but the effect of the pressure inside the reaction chamber is also investigated in (Imanaka et al., 2004). In the case of N_2:CH_4 mixtures, the 90:10 ratio is widely favored. Samples produced from mixtures with different CH_4/N_2 ratios are analyzed by GC–MS after a 750°C pyrolysis by (Coll et al., 2013). They however do not find any qualitative difference among the pyrolysates. They also compare the Huygens ACP experiment data with their results – obtained from pyrolysis of four kinds of samples: hydrogen cyanide polymer, solid hydrocarbons (polyethylene and anthracene), and tholins synthetized with cold and hot plasmas. The plasma is "cold" when the plasma heating does not significantly alter the temperature of the neutral gas. Coll et al. conclude that tholins produced in a cold plasma are the most similar analogues to Titan's aerosols regarding the volatiles released during pyrolysis.

Analysis conditions represent an additional variable, in terms of choice of chromatographic column (e.g. CPSil5-CB (Coll et al., 1998), DB-1 and RTX-Wax (McGuigan et al., 2006), PoraPLOT Q (Buch et al., 2006; Coll et al., 2013; Pietrogrand et al., 2001) and DB-5 (Ehrenfreund et al., 1995; Khare et al., 1984)) as well as of column temperature program, pressure conditions or pyrolysis temperature. These parameters are decisive for the kind of molecules, which are analytically detectable (polar/non-polar, heavy/light) with GCMS analysis. Lastly, the choice of pyrolyzer is important in the thermal decomposition process from solid to gas phase. Some pyrolyzers are indeed limited in the reachable pyrolysis temperature, as are the Curie point pyrolyzers. The geometry of the pyrolyzers and the residence-time of the pyrolysates are also variable, leading to a different recombination of species inside the oven (Moldoveanu, 1998). All these varying parameters explain the heterogeneity of the published studies.

Considering the disparity in the nature of the samples and in the analytical conditions used in previous studies, we carry out a systematic analysis of tholins produced in well-constrained pyr-GCMS conditions. Besides determining the composition and structure of these analogues of Titan's aerosols, the major objectives of this study are:

(i) To determine the variability in the tholins molecular composition for samples produced with different initial gas mixtures (methane concentrations between 2% and 10%) in the same conditions and with a given experimental device. The influence of the methane concentration on the tholins chemical composition has been highlighted in Sciamma-O'Brien et al. (2010) and Pernot et al. (2010). Sciamma-O'Brien et al. (2010) carried out elementary analyses on tholins samples synthesized with the PAMPRE experiment in 2010. They showed that the C/N ratio increases when the CH_4 concentration increases. In Pernot et al. (2010) a study of the tholins soluble fraction by high-resolution mass spectrometry showed an increase in the number of methylene (-CH_2-) groups with regard to nitrogen-bearing groups and a higher