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Structural Analysis of Titan's Tholins by Ultra-High Resolution Mass Spectrometry

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Abstract

Ultra high resolution mass spectrometry is used to analyze the chemical structure of tholins, laboratory analogues of Titan aerosols. Analysis of the fragmentation patterns allows retrieving some generic rules for the fragmentation of specific functional groups. These rules will be used as a basis to interpret the results of the tholins MS/MS experiments and will lead us to possible structures for the tholins.

1. Introduction

The structure, composition and formation processes of the aerosols constituting Titan's haze are largely unknown. In situ chemical analysis by the Huygens probe proved to be unsuccessful and remote optical data do not allow retrieving information about their molecular structure. As a consequence, analogues (called Titan tholins) are produced in laboratories by depositing energy in a gas mixture of nitrogen and methane. Tholins have been extensively analyzed with various analytical methods (IR, UV and Raman spectroscopy, NMR, pyrolysis-GC/MS, etc.) and appear to be hydrogenated carbon nitrides with a very complex structure [1].

Tholins react rapidly in ammonia-water solutions at low temperature, producing complex organic molecules containing both oxygen and altered nitrogen functional groups [2]. On Titan, aerosols sediment to the surface where they could react readily in transient aqueous pools that might be generated by impacts and volcanic processes. It is therefore of potential prebiotic interest to further characterize the laboratory analogues of these aerosols.

2. Experimental

While the techniques mentioned above provide information on the bulk tholins, very-high resolution mass spectrometry (HRMS) is necessary to determine the atomic composition of each individual molecule making up the samples [3]. Moreover, tandem mass spectrometry (MS/HRMS) experiments can provide complementary information on the functional group inventory in tholins [4]. However, the MS/HRMS fragmentation spectra gathered so far are insufficiently complete to allow the derivation of structural information. Based on these previous works, we propose here a systematic HRMS and MS/HRMS study in order to provide a more coherent and complete characterization of the structure of the molecules making up the soluble fraction of the tholins. Our tholin samples are synthesized in N_2-CH_4 gas mixtures with various CH_4 concentrations in a cold plasma discharge. The tholins are dissolved in CH_3OH [4, 5] and the soluble fraction is injected in a Fourier Transform LTQ-Orbitrap mass spectrometer by ElectroSpray Ionization (ESI). This produces protonated (positive mode) and deprotonated (negative mode) ions. Several ions in the mass range of 150-300 u are selected and used as precursor ions in tandem MS/HRMS experiments. Collision Activated Dissociation (CAD) with He as collision gas in a quadrupole ion trap and High Collision Dissociation (HCD) with Ar as collision gas in an octopole are used to perform MS/HRMS experiments.

3. Results

The mass spectra obtained with the LTQ-Orbitrap for solutions of tholins show that they are composed of many complex organic molecules. Those mass spectra are much more complex than HCN polymers, which we have analyzed with the same techniques [6]. Among the organic molecules which have been identified, tholins were found to contain 18 molecules with molecular formulae corresponding to biological amino acids and nucleotide bases (see communication from Hörst et al. at this conference). GC-MS measurements have confirmed the structure of seven: adenine, cytosine, uracil, thymine, guanine, glycine and alanine. With the LTQ-Orbitrap, MS/HRMS spectra have been recorded for the most intense peaks. Figure 1 shows an example of MS/HRMS spectrum of $C_9H_{10}N_9^+$ ions (m/z 244) obtained from a tholin sample synthesized from a mixture of N_2/CH_4 (98:2). The parent ion ($C_9H_{10}N_9^+$) fragments into three major daughter ions, corresponding to the loss of neutral NH_3, HCN and NH_2CN.

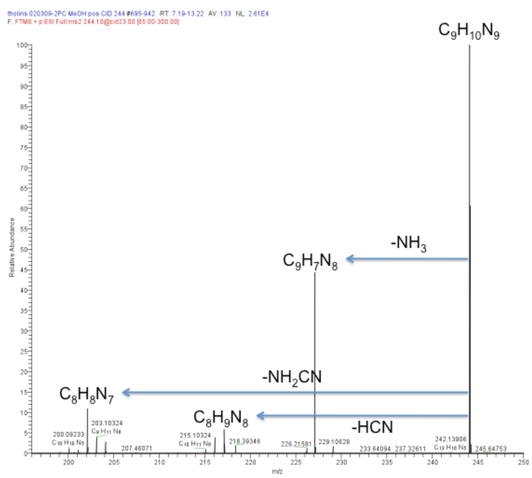

Figure 1: Typical ultra-high resolution MS/HRMS (CAD) mass spectrum of $C_9H_{10}N_9^+$ ions (m/z 244) coming from a tholin sample.

Tandem mass spectrometry of standard molecules of general formula $C_xH_yN_z$ having structures (aliphatics, aromatics, heterocycles) and chemical functionalities (azines, nitriles, imines, amines, etc.) similar to those expected in the tholins have been performed.

The analysis of the fragmentation patterns allows retrieving some generic rules for the fragmentation of specific functional groups:

•The fragmentation efficiency is related to the stability of the molecule. Aliphatic molecules fragment easily while cyclic and aromatic molecules do not fragment much.

•Aliphatic units lose HX readily (X = NH_2, CN)

•When NH_2 is linked to an aromatic, HCN (27 u) is lost rather than NH_3 (17 u).

•The loss of CH_3CN (41 u) occurs when a substituted heterocyclic structure is present.

•The loss of NH_2CN (42 u) is often related to guanidine.

These rules will be used as a basis to interpret the results of the tholins MS/MS experiments and will lead us to possible structures for the tholins.

4. Conclusion

Tholins have been shown to be composed of many complex organic molecules, mostly with nitrogen insertion. They are much more complex than HCN polymers.

These results highlight the importance and necessity of very-high mass resolution, accurate mass measurements and tandem mass spectrometry (MS/HRMS) experiments for a more coherent and in-depth characterization of complex organic solids. In the context of a return to Titan, development of space borne ultra-high resolution ($m/\Delta m > 10^5$) mass spectrometers capable of *in situ* sampling of the atmosphere is mandatory.

Acknowledgements

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