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High resolution mass spectrometry of Tholins: comparison with HCN polymers

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Abstract

Tholins, the analogues of Titan aerosols, are very enigmatic materials. This work presents the results of our efforts to understand their molecular and chemical composition by comparing them with other material with similar atomic content: HCN polymers, which are thought to be of relevance in comet composition.

Introduction

Titan aerosols are the result of a complex chemical growth, starting by the activation of molecular Nitrogen and Methane, proceeding into a molecular growth clearly visible in the INMS (Ion Neutral Mass Spectrometer) mass spectra [1], and eventually leading to macroscopic material, which slowly sediments in the atmosphere of the satellite, and leading to its brownish haze aspect.

As the aerosols' production and composition are very difficult to study from space or from Earth, a strategy of analogue synthesis was developed in the 80's. Basically, the production of solid samples (called tholins) occurs pretty easily provided that some gas mixture containing molecular Nitrogen and methane is maintained in a plasma, an arc, or exposed to UV light, for sufficient time.

Tholins are complex mixtures of molecules of the general composition HxCyNz [2]. Another type of molecules with the same atomic composition, and of relevance in astrophysics, are HCN polymers, thought to be present in cometary ices and to be at the origin of complex molecules, of potential prebiotic character [3]

Though these materials have been synthesised and studied for almost 30 years, there is still no clear explanation on how they are produced, what controls their final composition, and how they grow in the medium.

Mass spectrometry at ultra high resolution has already been applied to the study of tholins with great success [4]. This experimental method allows ascribing a stoechiometry to each molecule present in the mixture, and build some correlations in the spectra to disentangle and derive some rules for the molecular structures that are present.

Method

We have studied tholins produced in the Pampre reactor [5], and we have compared their mass spectra with those of polyHCN, produced at LISA [6]. The tholins result from a cold plasma discharge in a mixture of either 90%-10% or 98%-2% of nitrogen-methane, respectively. The HCN polymer results from ammonia catalysed polymerization in liquid HCN. The sample preparation was the same for both: solubilisation in methanol of the solid sample and Electrospray ionization in order to transfer to the mass spectrometer protonated or deprotonated molecules, without dissociation.

The mass spectra were recorded with the LTQ Orbitrap XL instrument. This Fourier Transform instrument allows ultra high resolution mass spectrometry, and because of the mass defect, provides with the atomic content of each molecule identified in the mass spectrum. Further, collision induced dissociation in the LTQ ion trap provides structural analysis of ions.

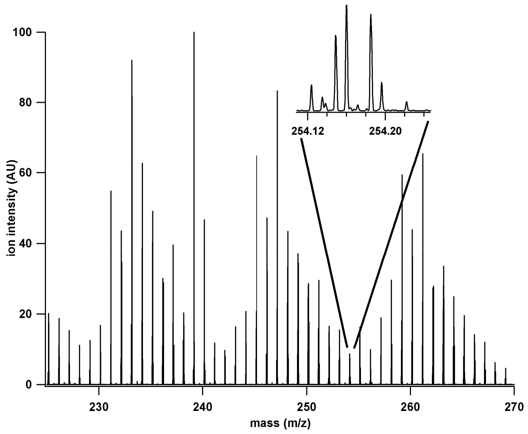

Figure 1: mass spectrum (mass range from 225-270) of tholins in the positive mode.

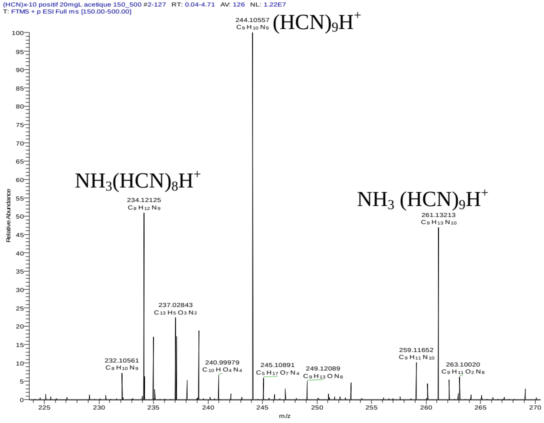

Figure 2 mass spectrum (range 225-270) of HCN polymer in the positive mode.

Results

If the solid samples are similar in aspect, and exhibit similar spectroscopy, the mass spectra are totally different, as shown in figure 1, showing a small section of mass spectrum of tholins, and figure 2, showing in the same section of a mass spectrum of HCN polymer. The Tholins mass spectrum is extremely congested, with one peak at each mass unit up to mass 500. When using high resolution, each of these peaks even appear as a mixture of molecules with different stoechiometry, as seen in the zoom of mass 254 in fig 1. This allows analysis of the molecular pattern making up this spectrum, and resulting in the broad clusters seen in Fig 1, spaced by about 13 to 14 amu. The HCN polymers exhibit almost exclusively peaks at the masses corresponding to (HCN)x moieties (i.e. peaks every 27 amu) from m/z = 54 (x = 2) to m/z = 972 (x = 36).

The collision induced mass spectra, and the systematic analysis of these ions helped us in deriving further information from these spectra, such as the huge content of amines in the HCN polymers, which is not obvious from their monomer structure. Further information concerns the oxidation of HCN polymers, which seems systematically in the form of carboxylic acid in the case of HCN polymers.

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