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## AN ATMOSPHERIC ORIGIN FOR A HCN-DERIVED POLYMER ON TITAN

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**Abstract.** Titan's haze is strongly suspected to be an HCN-derived polymer, but despite the first in situ measurements by the ESA-Huygens space probe, its chemical composition and formation process remain largely unknown. To investigate this question, we simulated in the laboratory, the atmospheric haze formation process. We synthesized analogues of Titan's haze, named Titan tholins, in an irradiated N<sub>2</sub>-CH<sub>4</sub> gas mixture, mimicking Titan's upper atmosphere chemistry. HCN was monitored in situ in the gas phase simultaneously with the formation and evolution of the haze particles. We show that HCN is produced as long as the particles are absent, and is then progressively consumed when the particles appear and grow. This work highlights HCN as an effective precursor of Titan's haze and confirms the HCN-derived polymer nature of the haze.

Keywords: HCN-polymers, microphysical evolution

### 1 Introduction

The largest satellite of Saturn, Titan, has a thick atmosphere based on N<sub>2</sub> and CH<sub>4</sub>. The photochemistry of N<sub>2</sub> and CH<sub>4</sub> leads to the formation of complex organic molecules, up to the formation of solid aerosols, observed under the appearance of an orange opaque haze by the Voyager 1 and Cassini/Huygens missions.

In-situ measurements by the Huygens probe (Israël et al. 2005), and laboratory experiments synthesizing Titan-like aerosols (called tholins), have revealed HCN as one of the main chemical signatures extracted from aerosols. This nitrile compounds has been detected in the gaseous phase, in Titan's atmosphere.

The objective of this work is to study in the laboratory if HCN is indeed a precursor to aerosol formation. Laboratory experiments were conducted using a dusty plasma reactor (Szopa et al. 2006) simulating the photochemistry of the Titan atmosphere, and initiating the formation of Titan-like organic aerosols (tholins) and associated gas-phase chemistry. In the present work, we simultaneously study the temporal evolution of HCN in the gas phase and the formation and growth of Titan tholins.

### 2 Context

#### 2.1 Literature citations

During its passage near Titan, the IRIS infrared spectrometer on board the Voyager 1 spacecraft detected nitrile compounds, including HCN, in its atmosphere (Liang et al. 2007). The latter is formed by EUV photochemistry based on methane and nitrogen.

Titan is also surrounded by an organic photochemical haze, which has been probed by the DISR, ISS, and UVIS instruments aboard the Cassini/Huygens space mission (Liang et al. 2007; Tomasko et al. 2008). The production of these haze nanoparticles starts in the upper atmosphere at 1000 km altitude (Waite et al. 2007). After their formation, they slowly sediment towards the surface of Titan during several years (Lavvas et al.

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2011) and are suspected to undergo chemical and microphysical evolution processes during their descent (Lavvas et al. 2012).

Their chemical composition was studied by the Huygens spacecraft during its landing through the atmosphere of Titan in January 2005 (Israël et al. 2005). HCN was found to be one of the main chemical signatures extracted from the aerosols after their pyrolysis and analysis by gas chromatography coupled to Mass spectrometry. Laboratory experiments have confirmed the possible contribution of HCN to Titan aerosols. Pyrolysis of Titan aerosol analogs, combined with GC-MS analyses identified HCN as a systematic pyrolytic fragment (Coll et al. 2013; Morisson et al. 2016; Khare et al. 1984), but Titan tholins were also found to be more complex than pure HCN polymers (Vuitton et al. 2010; Bonnet et al. 2013). This converging evidence points to a probable polymeric HCN derivative structure for Titan aerosols.

## 2.2 Experimental simulation

Titan aerosol analogues are formed using the PAMPRE experiment (Szopa et al. 2006). PAMPRE is a reaction chamber, where a cold capacitively coupled radio frequency plasma is ignited at low pressure (0.9 mbar). A gas mixture of 95% N<sub>2</sub> and 5% CH<sub>4</sub> is injected into the reactor. Then a discharge is initiated, photolysing methane and nitrogen, and simulating photochemistry on Titan.

In this work, the gas flow rate was optimised to increase the residence time of the gas mixture in the reactor as much as possible. The chemical growth of the solid particles is thus favoured, making it possible to simultaneously follow the formation and evolution of the particles, as well as the co-evolution of the gas mixture composition.

## 3 Results

### 3.1 Morphology analysis of tholins by scanning electron microscopy

The formed samples were observed by scanning electron microscopy (SEM field emission gun).

Different stages of growth are observed in the images. In the first stage, the so-called primary nanoparticles coagulate with each other and form aggregates (Fig.1). These aggregates continue to grow into single spherical grains of 1.5 µm in diameter (Fig. 1). Subsequently, these micrometric spherical grains evolve by agglomerating.

### 3.2 Time evolution of the gas phase by mass spectrometry

The evolution of the N<sub>2</sub> - CH<sub>4</sub> gas phase allowing the production of organic polymers (tholins), is observed by quadrupole mass spectrometry, particularly for the masses corresponding to methane (m/z=16) and hydrogen cyanide (m/z=27).

Several phases are highlighted in the experiment (Fig. 2). Different phases of methane consumption (Fig. 2, red curve), with distinct decreasing slopes (on the logarithmic scale), associated in a first time with the ignition of the plasma discharge, in a second time with the formation of the primary nanoparticles, and in a third time with the agglomeration and growth of these nanoparticles. Finally, the stationary state is reached, by an equilibrium between particle growth and methane consumption.

In parallel, HCN is first produced, depending on the dissociation of the major components. Then it is progressively consumed in two distinct steps, in correlation with the appearance of the powders and their growth (Fig. 2, blue curve).

### 3.3 Figures

## 4 Conclusions

For conclusion, the observations made, highlight that the HCN formed during the simulation of Titan's photochemistry, is one of the precursors of Titan-like aerosols formed at low flows, interacting since their formation

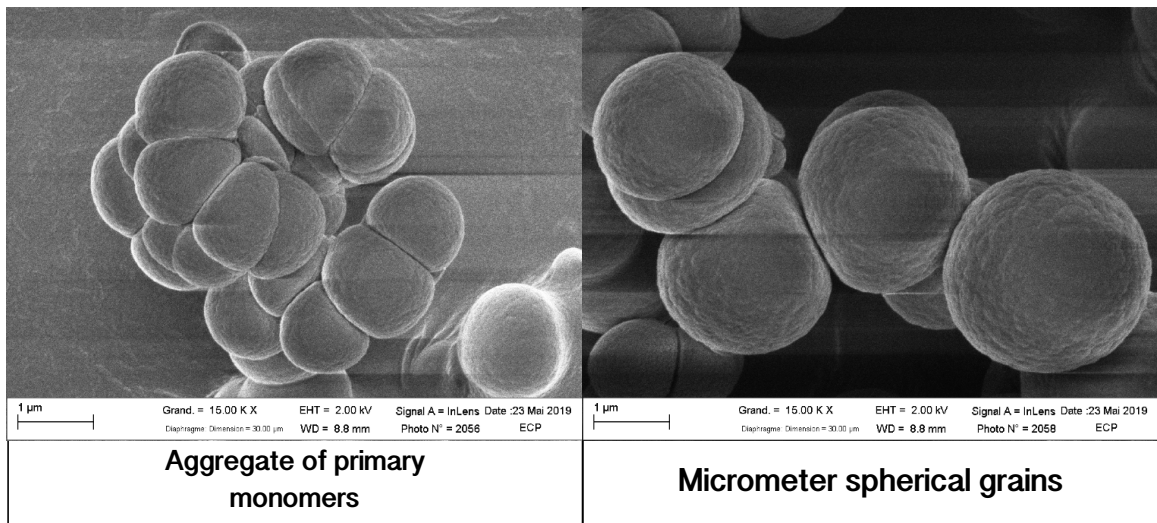


Fig. 1. SEM pictures of sample

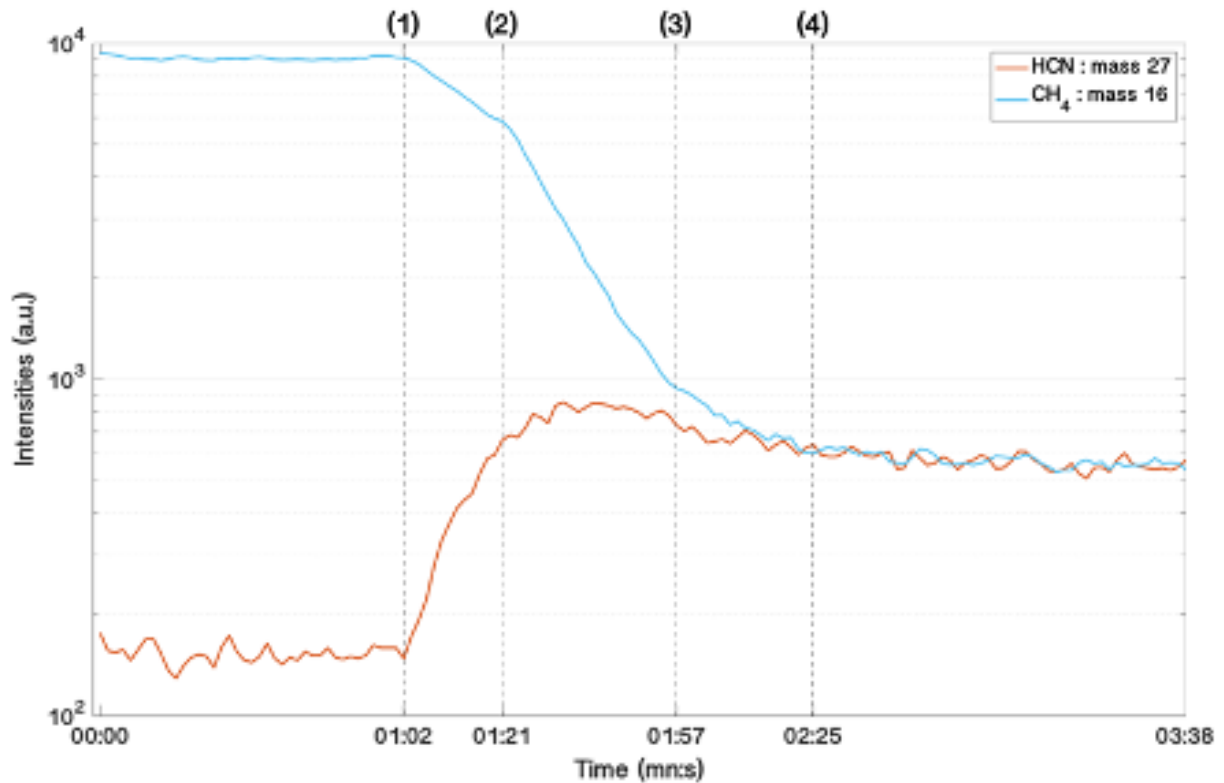


Fig. 2. Time evolution of the masses  $m/z$  16 ( $\text{CH}_4$ ), 27 ( $\text{HCN}$ ) of the gas phase present during the experiment

and then during their growth (Perrin et al. 2021).

This assumption is also made in the microphysical evolution model of aerosols residing in Titan's atmosphere by (Lavvas et al. 2012), where the predicted aerosol growth is similar in some respects, to that observed experimentally in this study.

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