Formation of adenine from the soft X-ray photo-irradiation of N_2-CH_4 ice.

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Introduction

Titan, the largest satellite of Saturn, has an atmosphere chiefly made up of N_2 and CH_4, and including many simple organic compounds. This atmosphere also partly consists of hazes and aerosols particles which shroud the surface of this satellite, giving it a reddish appearance. As a consequence of its high surface atmospheric pressure ($\sim$ 1.5 bar) the incoming solar UV and soft X-ray photons are mostly absorbed allowing virtually no energetic photons to reach the surface. However, during the last 4.5 gigayears, the photolysed atmospheric molecules and aerosol particles have been deposited over the Titan surface composed by water-rich ice (80-90 K) delivered by comets. This process may have produced in some regions a ten meter size, or even higher, layers of organic polymer [1], also known as "tholin" [2].

In this work investigate the chemical effects induced by soft X-rays in the Titan aerosol analog. The experiments have been performed inside a high vacuum chamber coupled to the soft X-ray spectroscopy (SXS) beamline at the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil.

Experimental methodology and results

Briefly, a gas mixture simulating the Titan atmosphere (95% N_2, 5% CH_4) was continuously deposited onto a polished NaCl substrate previously cooled at 13-14 K and exposed to synchrotron radiation (maximum flux between 0.5-3 keV) up to 73 hs.

A small fraction of water and CO_2 was also continuously deposited on the frozen substrate simulating thus, a possible heavy cometary delivery at Titan. The total energy deposited on the sample was about $\sim 10^{12}$ erg. *In-situ* sample analysis were performed by a Fourier transform infrared spectrometer (FTIR) during the irradiation and during the sample slowly heating to room temperature. The IR analysis has shown several organic molecules created and trapped in the ice, including the reactive cyanate ion ONC^-, nitriles, and possibly amides and esters (Fig. 1a).

After the irradiation phase, the sample was slowly heated up to room temperature, and another set of IR spectra were collected to follow the chemical changes promoted by thermal heating. A similar heating could be achieved locally at Titan surface during a comet impact or volcanism events. Next, the chamber was filled with dry nitrogen up to atmosphere pressure. The NaCl substrate, with the brownish-orange organic residue (tholin), was disconnected from the sample holder, conditioned into a sterile vial and sent to chromatographic (GC-MS) analysis revealing the presence of adenine ($C_5H_5N_5$), one of the constituents of DNA molecule. This prebiotic compound was also detected by proton nuclear magnetic resonance (NMR) analysis of the produced tholin. The complete description of the experimental setup and results can be found elsewhere [3].

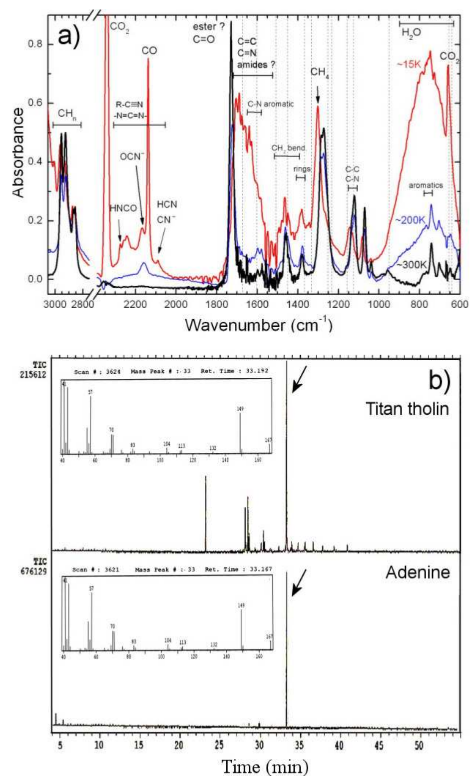

Figure 1: (a) Comparison between FTIR spectra of 73 h irradiated sample at 15, 200, and 300 K. (b) Total-ion current chromatogram of processed the Titan tholin and of the adenine standard.

To our knowledge the present work is the first experiment employing photons in which adenine was synthesized in an primitive atmosphere simulation. The interaction between soft X-rays and matter produce energetic secondary electrons which could be essential for adenine synthesis, since adenine have been observed in previous experiments involving discharges and electron bombardment [4-6].

In this work no amino acids or other nucleobases (guanine, cytosine, uracil or thymine) were observed in the residues from chromatographic or NMR analysis. This could be attributed by the small radiation resistance of theses species to soft X-rays [7]. Recently, Pilling and collegues [8] have observed from experiments involving the photodegradation solid phase and gas-phase biomolecules by soft X-rays, that adenine is at least 10 times less radiation sensitive than uracil and thousand times more resistent than amino acids.

Recently measurements done by Cassini spacecraft have revealed that Titan is not in synchronous rotation (same face to the planet) with Saturn indicating a possible internal ocean of liquid water[9]. If Titan have experienced a warm period in the past, promoted by external (e.g. comets impacts, Saturn magnetic field and tide effects) or internal (e.g. vulcanism, intense radioactive decay) forces to make liquid its water-ammonia ices some prebiotic molecules precursors cloud have been hydrolyzed and a primitive life could have had a chance to flourish there. In the other hand, in the very far future, when the sun becomes a magnificent red-giant and fill the solar system up to Earth orbit, Titan land surfaces may changes to liquid-land surfaces allowing these prebiotic compounds, produced and processed by radiation and energetic particles over a billions years, to react. When this time comes, life will have another chance to arise like happened in the primitive Earth.

Summary

In this work, we present the chemical alteration produced by the interaction of soft X-rays (and secondary electrons) on Titan aerosol analogs. The experiments simulate roughly 7×10^6 years of solar soft X-ray exposure on Titan atmosphere. Thermal heating of frozen tholin drastically changes its chemistry, resulting in an organic residue rich in C-C and C-N aromatic structures.

On Titan, the processed aerosols will be deposited along the time at the surface or at the bottom of lakes/rivers, leaving with them newly formed organic species. Gas chromatography analysis of the organic residue at room temperature has shown that among several nitrogen compounds, adenine, is one of the most abundant species produced due to irradiation by soft X-rays. This confirms previous studies suggesting that the organic chemistry in the Titan atmosphere and on the surface should be complex, being rich in prebiotic molecules such as adenine and amino acids (or its precursors species). Molecules such as these on the early Earth have found a place that allows life (as we know) to flourish, a place with liquid water.

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