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Potential chemical evolution of aerosols on Titan's surface: some new results on Titan's tholins

P. Coll (1), O. Poch (1), S. I. Ramirez (2), A. Buch (3), C. Brassé (1) and F. Raulin (1)
(1) LISA, Univ. Paris-Est and Paris Diderot, Créteil, France (2) CIQ, Univ. Morelos, Cuernavaca, Mexico (3) LPGM, Ecole Centrale Paris, Chatenay-Malabry, France (pcoll@lisa.u-pec.fr)

Abstract

Titan's environment hosts a complex organic chemistry that can be investigated from Earth-based laboratory experiments. One of the key astrobiological questions of Titan's environment is the fate of the organic aerosols produced in the atmosphere, after they are deposited on the surface. In the present study, we report the geological structures these aerosols may encounter in the light of the last observations of the Cassini-Huygens mission. We chose to quantify the production of some astrobiologically interesting molecules in putative ammonia-water bodies likely to be present at the surface or subsurface of Titan, as crater melt pools or cryolavas.

After aerosol analogues (tholins) synthesis and surface hydrolysis simulation, some resulting products were identified and quantified. Tholins were found to be very reactive toward an oxygen source. Urea was identified as the main product of Titan's tholins hydrolysis in ammonia-water solutions, with a production yield in mass, ranging from 6 to 12% at 279 K after 10 weeks. Several amino acids - alanine, glycine and aspartic acid - and perhaps the uracil nucleobase were also produced with yields from 0.001 to 0.4%. The determination of production yields carried out by the present study is a major step into the characterization of potential aerosols evolution on Titan.

1. Introduction

Deposition of organic aerosols on Titan's surface, where fluvial, aeolian, and cryovolcanic as well as cratering processes are acting (Fig. 1), may lead to their subsequent chemical evolution. Experimental assessment of this evolution on Titan's diverse surface is of major interest in the field of the post-Cassini-Huygens data treatment and preparation of future flagship missions. In this context, we focused our work on this key question: may Titan's aerosols efficiently interact with the surface to produce molecules of astrobiological interest?

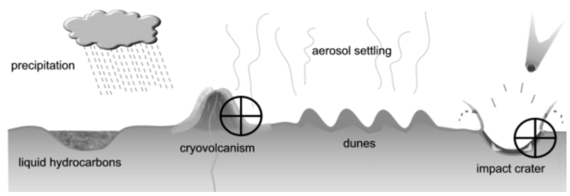

Figure 1: Review of geological formations identified or potentially identified on the surface of Titan. The priority targets considered in this study are cryovolcanic flows and impact craters melt pools.

2. Objective

Previous experiments have shown that Titan's tholins are readily hydrolyzed by acidic liquid water into amino acids at temperatures ranging from 70 °C to 100 °C (see [1] and [2]). Recently, efforts have been done to conduct tholins hydrolysis experiments under conditions more representative of those found on Titan, for example in subcrater melt pools or cryomagma ([3], [4], [5] and [6]). By using a combination of high resolution mass spectroscopy and tandem mass spectrometry fragmentation techniques, Neish et al. (2010) identified four amino acids after tholins hydrolysis in a 13 wt % ammonia-water solution at 253 K for 1 year [5]. Moreover, Ramírez et al. (2010) performed a derivatization reaction using N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA), solvated in dimethylformamide (DMF), on alkaline hydrolyzed tholins kept at 269 K, 153 K and 96 K for 10 weeks at different ammonia concentrations, from 3 to 25 wt % NH_4OH [6]. After a GC-MS analysis they detected seven amino acids as well as urea. Along with the identification of the hydrolysis products, Ramírez et al. (2010) performed for the first time, the quantification of the amino acids and urea synthesized under the basic hydrolysis at temperatures representative of Titan's surface, and compute their hydrolysis yields [6]. This first quantification study calls our attention to the improvement of some steps in our experimental protocol and into a closer analysis of our results. Consequently, we decided to carefully analyze the different steps related to the computation of hydrolysis yields, taking into account some concerns, revealed by our first study.

3. Experimental

After synthesis by irradiation of a N_2:CH_4 (98:2) gas mixture by a cold plasma discharge, aerosol analogs were recovered, partitioned in several 10.0 mg samples and kept at specific conditions simulating Titan's surface conditions during 10 weeks. Then they were prepared for a chemical quantitative molecular analysis (Fig. 2). This derivatization step was performed to allow the analysis of the targeted molecules with the GC-MS system. This derivatization step is needed to increase the volatility of the refractory and polar organic compounds and facilitate their analysis by the gas chromatograph (see [7] for details).

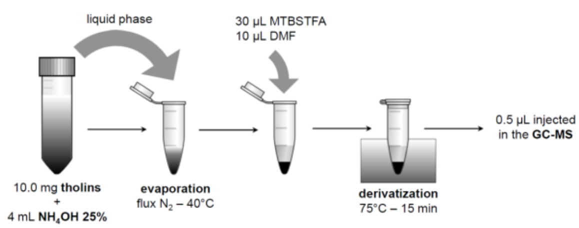

Figure 2: Preparation protocol before analysis of the solutes contained in the tholins hydrolysis solutions.

4. Results overview

We put in evidence the production of alanine, glycine, urea and aspartic acid in ammonia solution (Table 1). Their yields are higher than those obtained in water solution. Tholins kept in 25% NH_4OH solution for ten weeks undergo a higher incorporation of oxygen that tholins kept in distilled water, at the same temperature (279 K). A higher production of glycine, ~ 7 to 8 times greater, and aspartic acid, ~ 2 times greater, is observed under hydrolysis with ammonia compared to hydrolysis performed in distilled water, at 279 K. There is also a significant increase in the production of alanine, ~ 2 times more, its presence in the reference ammonia solution being negligible. Notably, 926 ± 12 µg of urea are produced during ammonia hydrolysis at 279 K compared to 253 K, making urea one of the major products, with production yields ranging from 6 to 12%. By comparison the yield was nearly zero (with an upper limit of 3%) for tholins placed in distilled water, revealing that ammonia accelerate the evolution of Titan's tholins [7].

	Tholins + water at 279 K	**Tholins + NH_4OH at 279 K**	**Tholins + NH_4OH at 253 K**
Alanine	no data	0.02-0.03 %	0%
Glycine	0.04-0.06 %	0.3-0.4 %	0-0.004 %
Urea	0-3 %	6-12 %	0-2 %
Uracil	0%	0.0006-0.0009 %	0%
Aspartic Acid	0.0016-0.002 %	0.003-0.004 %	0-0.0003 %

Table 1: Production yields of alanine, glycine, aspartic acid, urea, adenine and uracil in hydrolysis solutions of 10.0 mg tholins, after 10 weeks. For additional information, see [7].

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