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Detection and reactivity of Titan tholins in liquid hydrocarbons containing polar compounds

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Abstract

Tholins are complex organic materials produced via photolysis of methane and dinitrogen gases in Titan's upper atmosphere. These long-chained hydrocarbons sediment to the moon surface and interact with liquid hydrocarbons via methane rain [1], [2] and methane-ethane-nitrogen dominated lakes and seas [3]–[6]. However, preliminary studies have shown that tholins are only weakly soluble in non-polar solvents such as methane and ethane, and soluble in polar solvents [7]–[11]. We have decided to determine the solubility of Titan tholins in solutions of liquid hydrocarbons mixed with nitriles, such as acrylonitrile, acetonitrile, and hexane.

1. Introduction

Kawai et al. [12] and He et al. [13] detected amino acids (e.g. glycine, alanine) as products of solubility of tholins dissolved in polar solvents. Studies have found that the solubility of tholins increases as the polarity of the solvent increase [7]–[10]. We plan to determine the solubility of Titan tholins, as well as structurally similar compounds, in solutions of liquid hydrocarbons containing polar solvents, such as acrylonitrile and acetonitrile dissolved in hexane solutions.

2. Experimental Methods

Acetonitrile, acrylonitrile, hexane, and mixtures of acetonitrile/hexane, acrylonitrile/hexane will be used as solvents. While methane and ethane are the abundant liquids on Titan, both are in the gas phase under room temperature and pressure. Therefore, hexane, liquid in ambient conditions, will be used as a non-polar alkane solvent instead.

2.1 Tholin Production

This study uses a cold plasma discharge (approx. 27mA) simulating charge particle radiation interacting in a 90% nitrogen and 10% methane gas

mixture (simulating Titan's atmosphere) to synthesize Titan tholins (as seen in Figure 1). Chamber conditions of 0.5 Torr to 3.00 Torr were maintained at room temperature for approximately 3 days with a continuous flow of the N_2 - CH_4 gas mixture.



Figure 1: Technics Hummer II sputtering chamber triggering a DC cold plasma discharge at 30mA that ionizes the Titan-simulated N_2 - CH_4 (90%-10%) gas mixture to produce tholins after several days.

Glass slides are positioned inside the sputtering chamber to collect tholin while synthesized (Figure 2). Approximately 200 mg of synthesized Titan tholins were produced from this process.

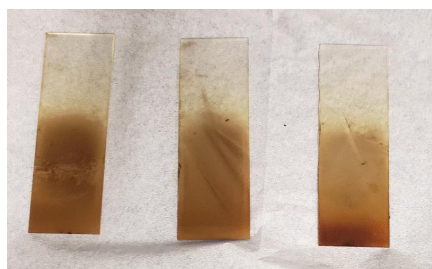


Figure 2: Tholins produced from cold plasma discharge using the experimental setup and conditions described earlier.

2.2 Solubility Experiments

We will first determine the solubility of tholins at three temperatures close to room temperature (248K, 273K, and 298K). The objective of this task is double: first, we want to calibrate the future experimental solubilities in liquid methane and ethane. Determining the solubility of tholins at room temperature will quasi-quantitatively inform on the solubilities to expect in the cryogenic solvents (typically if they are in the ppm or percent range). The second objective is to determine the kinetics of the dissolution process(es). Then, by determining the kinetics at the three different temperatures, we will be able to extrapolate to the cryogenic conditions in the chamber. At different times of the solubility experiment, we will sample a few microliters of the solutions for GC-MS measurements. In addition, the tholins before and after dissolution will be measured with FTIR (1 to 5.5 μm) and Raman spectroscopy to study the solid residue and compare them with standard spectra of tholins.

3. Summary and Conclusions

This study aims to investigate the prebiotic chemistry of Titan and the fate of tholins and production of complex organic molecules on the surface. As much as there has been extensive experimental work on the formation of tholins in Titan's atmosphere, as well as their potential hydrolysis, there is virtually no extensive study of their further reactivity with liquid hydrocarbons once deposited on the surface. We will present preliminary results obtained so far for this solubility study. The first and most straightforward significance of our work is to provide new solubility data on polar compounds in liquid hydrocarbons. Our second significance is to characterize the potential reactivity of tholins in the presence of liquid non-polar hydrocarbons with dissolved polar species. This could demonstrate the possibility for heterogeneous chemical reactions in exotic liquid solvents. Results of this study at room temperature will be used to constrain our future experiments of the solubility of tholins in liquid methane-ethane mixed with the same polar compounds at Titan's temperature and pressure. This future work will give insights into the habitability of Titan.

References

[1] E. P. Turtle *et al.*, "Rapid and extensive surface changes near Titan's equator: Evidence of April showers," *Science* (80-.), vol. 331, no. 6023, pp. 1414–1417, 2011.

[2] J. W. Barnes *et al.*, "Precipitation-induced surface brightenings seen on Titan by Cassini VIMS and ISS," *Planet. Sci.*, vol. 2, no. 1, pp. 1–22, 2013.

[3] A. Luspay-Kuti *et al.*, "Experimental constraints on the composition and dynamics of Titan's polar lakes," *Earth Planet. Sci. Lett.*, vol. 410, pp. 75–83, 2015.

[4] G. Mitri, A. P. Showman, J. I. Lunine, and R. D. Lorenz, "Hydrocarbon lakes on Titan," *Icarus*, vol. 186, no. 2, pp. 385–394, 2007.

[5] D. Cordier, O. Mousis, J. I. Lunine, P. Lavvas, and V. Vuitton, "An estimate of the chemical composition of Titan's lakes," *Astrophys. J.*, vol. 707, no. 2 PART 2, pp. 128–131, 2009.

[6] R. H. Brown *et al.*, "The identification of liquid ethane in Titan's Ontario Lacus," *Nature*, vol. 454, no. 7204, pp. 607–610, 2008.

[7] N. Carrasco *et al.*, "Chemical characterization of Titan's tholins: Solubility, morphology and molecular structure revisited," *J. Phys. Chem. A*, vol. 113, no. 42, pp. 11195–11203, 2009.

[8] N. Sarker, A. Somogyi, J. I. Lunine, and M. A. Smith, "Titan Aerosol Analogues: Analysis of the Nonvolatile Tholins," *Astrobiology*, vol. 3, no. 4, pp. 719–726, 2003.

[9] P. Coll *et al.*, "Experimental laboratory simulation of Titan's atmosphere: aerosols and gas phase," *Planet. Space Sci.*, vol. 47, no. 10–11, pp. 1331–1340, 1999.

[10] C. P. McKay, "Elemental composition, solubility, and optical properties of Titan's organic haze," 1996.

[11] C. He, G. Lin, K. T. Upton, H. Imanaka, and M. A. Smith, "Structural investigation of Titan tholins by solution-state ^1H , ^{13}C , and ^{15}N NMR: One-Dimensional and Decoupling Experiments," *J. Phys. Chem. A*, vol. 116, no. 19, pp. 4760–4767, 2012.

[12] J. Kawai *et al.*, "Titan Tholins as Amino Acid Precursors and Their Solubility in Possible Titan Liquidospheres," *Chem. Lett.*, vol. 42, no. 6, pp. 633–635, 2013.

[13] C. He and M. A. Smith, "Solubility and stability investigation of Titan aerosol analogs: New insight from NMR analysis," *Icarus*, vol. 232, pp. 54–59, 2014.