

Effective Dissolution of Aromatic Hydrocarbons from Organic Aerosols by Interactions with Liquid Methane on Titan. E. Hirai¹, Y. Sekine¹, N. Zhang¹, N. Natsumi², and H. Kagi³, ¹Earth & Life Sci. Inst. (ELSI), Tokyo Inst. Tech. (2 Chome-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, JAPAN, eight@elsi.jp), ²Dept. Earth & Planetary Sci., Univ. of Tokyo, ³Geochem. Res. Center, Univ. of Tokyo

Introduction: Titan has unique surface environments, where planetary-scale organic chemistry is proceeding. In Titan's thick atmosphere, organic aerosols are generated from N₂ and CH₄ via photo/ion-chemical reactions induced by solar UV and energetic particles from Saturn's magnetosphere [1]. These organic aerosols settle on the surface and may interact with liquid CH₄ [2], which could affect the morphology and composition of organic materials [3].

One possibility of chemical interactions between organic aerosols and liquid CH₄ on Titan includes a large size gap of organic materials on the surface. Titan's equatorial dunes are thought to be composed mainly of organic deposits, including organic aerosols, on the surface [4,5]. Nevertheless, dune particle size is suggested to be an order of 100 μm [6], while aerosols in troposphere are considered to be $\sim 0.1\text{--}1\text{ }\mu\text{m}$ of aggregate of 50-nm monomers [7], calling for a geological process responsible for coagulation of organic aerosols, for example, during wet-and-dry cycles of liquid CH₄.

Another possibility for interactions between organic aerosol and liquid CH₄ is the widespread presence of 5 μm -bright evaporites [8, 9, 10]. These evaporites tend to be present on paleo-lake/-sea deposits, exhibiting a characteristic absorption feature at 4.92 μm [11] similar to those of nitriles [12]. Benzene is also detected in a paleo-basin with a characteristic absorption feature at 5.05 μm [12]. These observations suggest that nitriles/benzene has once dissolved in liquid hydrocarbons on Titan; however, it is inconsistent with predictions by previous photochemical models, which suggested photochemically-produced acetylene and butane should be the major solutes in methane lakes to form evaporites [13]. This may imply that there could be an alternative source of nitriles and/or benzene to lakes of liquid hydrocarbons. One possibility is nitriles and/or benzene could have been provided from organic aerosols by dissolution into liquid CH₄.

Here we report our experimental results of interactions between Titan's organic aerosol analogs (Titan tholin) and liquid CH₄ at low temperatures comparable to Titan's surface (90–100 K). We investigated morphologic and compositional changes of Titan tholin due to interactions with liquid CH₄. We also analyzed the morphology and composition of evaporites formed after the evaporation of liquid CH₄.

Methods: We developed a liquid CH₄ generator,

in which liquid CH₄ can react with Titan tholin under controlled temperature conditions (Fig. 1). To separate reacted Titan tholin and evaporites, we set Titan tholin on Al substrates on a Ti mesh over a dent in the liquid CH₄ generator (Fig. 1). After immersing Titan tholin with liquid CH₄ at 90–100 K, liquid CH₄ is gradually evaporated using a mechanical pump at roughly constant low temperature. Evaporites of dissolved species remain on the bottom of the dent, and undissolved parts of Titan tholin remain on Al substrates on the Ti mesh.

Titan tholin was produced by cold plasma irradiation onto a gas mixture of 10% CH₄/N₂ at pressure of $\sim 200\text{ Pa}$ for 6 hours. We collected spherical particles of Titan tholin with diameter of 50–100 nm (Fig. 1a) on Al substrates in the cold-plasma reaction chamber.

After setting Titan tholin particles in the liquid CH₄ generator at temperatures of 90–100 K, CH₄ gas was introduced into the generator to produce liquid CH₄. We immersed Titan tholin with liquid CH₄ for 6 hours. After evacuation of CH₄, we collected residual Titan tholin on Al substrates and evaporites on the bottom of the generator. These samples were then analyzed using a field emission scanning electron microscope (FE-SEM), Fourier-transform infrared (FT-IR) spectrometer, and FT-IR equipped with an infrared microscope.

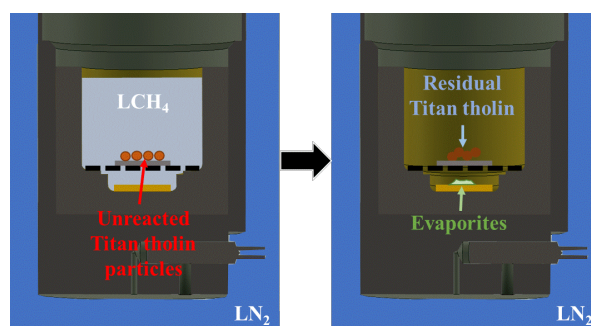


Figure 1. A schematic diagram of the cross-section of the liquid CH₄ generator during dissolution with liquid CH₄ (left). The black broken line represent a Ti mesh. After evaporation of liquid CH₄, residual Titan tholin and evaporites are collected (right).

Results & Discussion: Figure 2 shows typical FE-SEM images of unreacted Titan tholin (a), residual Titan tholin after reaction (b), and evaporites (c, d). After dissolution and subsequent evaporation, Titan tholin particles coagulate and grow to a few- μm aggregate (Fig. 2b). Particles seem to be chemically con-

nected with thick necks, suggesting that coagulation occurred via dissolution and precipitation of organic compounds at particle boundaries. There are little differences in individual particle size between unreacted and reacted Titan tholin, suggesting that the mechanism of coagulation is not Ostwald-ripening but solidification of dissolved organic compounds. We also found evaporite deposits with $\sim 10\ \mu\text{m}$ of diameter with a round and flat shape (Fig. 2 c). These evaporites frequently contain circular cavities with sub- μm size on the surface, suggesting that degassing of a trapped gas component occurred during evacuation. Plate-shape evaporites with cavities were also observed (Fig. 2d).

Figure 3 shows typical micro-IR spectra of these samples. Unreacted Titan tholin, residual Titan tholin, and evaporites exhibit generally similar absorption features. One remarkable feature of evaporites is a relatively intense absorption band at $1580\ \text{cm}^{-1}$, suggesting the possible high abundance of aromatic hydrocarbons existing in evaporites. Our results also show that absorptions assignable to nitriles at $2240\text{--}2180\ \text{cm}^{-1}$ are relatively weak in evaporites, compared with unreacted and residual Titan tholin (Fig. 2). The intensity ratio of absorptions caused by N-H bonds at $\sim 3320\ \text{cm}^{-1}$ relative to C-H bonds at $\sim 2950\ \text{cm}^{-1}$ was high in residual Titan tholin and low in evaporites. Our results suggest that aromatic hydrocarbons can be easily dissolved from Titan tholin into liquid CH_4 ; whereas, nitriles tend to be undissolved and remain in residual Titan tholin.

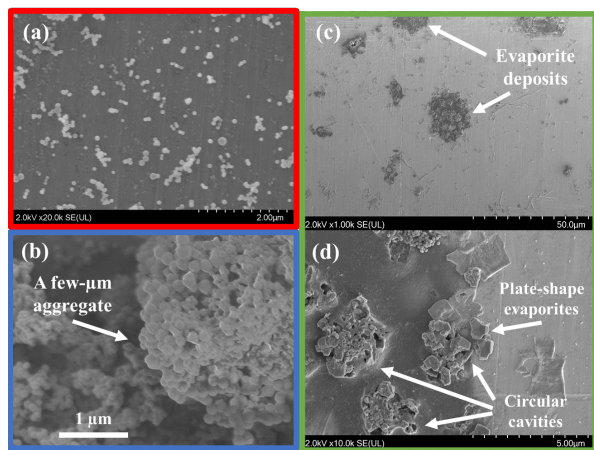


Figure 2. FE-SEM images of unreacted Titan tholin (a), residual Titan tholin (b), and evaporites (c, d).

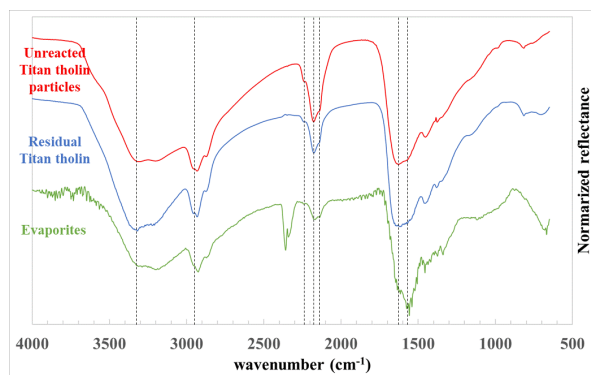


Figure 3. Representative IR spectra of each sample.

Implications for evaporites on Titan: Similar to our laboratory analog, in-situ observations in the upper atmosphere of Titan have suggested its organic aerosols contain aromatic hydrocarbons [14]. Our results indicate that these aromatic hydrocarbons in organic aerosols could be efficiently dissolved in liquid CH_4 , suggesting that organic aerosols would be a source of aromatic hydrocarbons (e.g. benzene) for evaporites on Titan [15]. Undissolved parts of organic aerosols would coagulate via wet-and-dry cycles of liquid CH_4 , possibly explaining a size gap of organic particles between aerosols and dune particles. Our results also suggest that dissolution and coagulation of organic aerosols would proceed efficiently in a short time period (e.g., within 6 hours in our experiments) even at Titan's surface temperatures, highlighting overlooked importance of liquid-organic interactions for chemical evolution on Titan.

References: [1] Hörst S. M., (2017) *J. Geophys. Res. Planets*, 122, 432-482. [2] Yu X. et al., (2020) *The Astrophys. J.*, 905, 88. [3] Cable M. L. et al., (2012) *Chem. Rev.*, 112, 1882–1909. [4] Lorenz R. D. et al., (2008) *Geophys. Res. Lett.*, 35, L02206. [5] Lopes R. M. C. et al., (2020) *Nature astronomy*, 4, 228-233. [6] Lorenz R. D., (2014) *Icarus*, 230, 162–167. [7] Tomasko M. G. et al., (2008) *Planet. Space Sci.* 56, 669-707. [8] Mackenzie S. M. et al., (2014) *Icarus* 243, 191-207. [9] Barnes J. W. et al., (2011) *Icarus* 216, 136–140. [10] Moore J. M. and Howard A. D. (2010) *Geophys. Res. Lett.*, 37, L22205. [11] Mackenzie S. M. and Barnes J. W., (2016) *The Astrophys. J.* 821, 17. [12] Clark R. N. et al., (2010) *J. Geophys. Res.*, 115, E10005. [13] Cordier D. et al., (2013) *Icarus*, 226, 1431–1437. [14] Waite J. H. et al., (2007) *Science*, 316, 870. [15] Malaska M. J. and Hodyss R., (2014) *Icarus*, 242, 74-81.