INTERACTIONS BETWEEN ETHYLENE AND BENZENE UNDER TITAN CONDITIONS.

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Introduction: Titan's lakes of ethane/methane offer a unique laboratory for prebiotic chemistry [1]. Titan's nitrogen-based atmosphere and active methane hydrological cycle allow for interactions among many hydrocarbons in both the solid and liquid phase [2].

Since *Dragonfly* was selected for flight, there has been an increased interest in the composition of Titan's surface, as well as the interactions that occur between/among molecules. Previous studies have investigated possible evaporites [3,4] and co-crystals [5-9], which have been confirmed under experimental Titan surface conditions. Evaporites form when a solid compound precipitates from a liquid after evaporation [4]. Co-crystals are crystalline solids that are comprised of two or more compounds in a fixed ratio and exhibit a unique crystalline structure [8,9]. Evaporites may be present in/around empty lake basins. Co-crystals could also form in the lakes of Titan, where many organic compounds could interact.

Ethylene (C_2H_4) and benzene (C_6H_6) have been detected in the atmosphere, and may condense and interact on the surface of Titan [10-12]. Acetylene and ethane have already been verified to form co-crystals with benzene at cryogenic conditions [5,9], however, to the best of our knowledge an ethylene co-crystal has not been observed under Titan conditions. The objective of our study is therefore to determine if co-crystals of benzene and ethylene can form under Titan's surface conditions. Because the freezing point of ethylene (104 K) is close to Titan's surface temperature (~89 K - 94 K), and the freezing point of benzene (278 K) is much higher, these interactions may occur as a solid-liquid interaction, with benzene in the solid phase and ethylene in the liquid phase.

Methods: The Titan Surface Simulation Chamber (TSSC) at the University of Arkansas [13] was used to perform these experiments under Titan surface conditions (93 K, 1.5 bar N_2). The temperature is maintained by pumping liquid nitrogen through cryogenic lines that wrap around the chamber and temperature control box (TCB), which houses the experiment. The pressure is maintained by pumping nitrogen gas throughout the chamber and TCB. Fourier transform infrared spectroscopy (FTIR) spectra, mass, temperature, and optical images are acquired during each experiment. The wavelength range provided by the FTIR spectrometer is from 1 to 2.5 µm.

Benzene is deposited directly into the chamber above the sample dish, after vapor saturation of a nitrogen gas flow with liquid benzene at room temperature. Benzene deposits onto the sample dish in a snow-like state (solid phase). After the benzene has been deposited, the chamber is cooled until it reaches the liquid phase of ethylene (169 K). Ethylene is then introduced to the condenser via gas lines, where it condenses into a liquid. The solenoid valve is opened, allowing the ethylene to drip onto the dish, on top of the solid benzene. The chamber is then further cooled to Titan-relevant temperatures, collecting data as it cools.

Results and Discussion:

FTIR Spectra: FTIR spectra acquired on the benzene and ethylene mixture (Fig. 2) do not exhibit significant differences from the pure spectra (Fig. 1). No new spectral bands formed, only the combination and superposition of ethylene and benzene spectra. As the temperature reached that of Titan's surface, the overall reflectance decreased. The reflectance then increased as the mixture was warmed back up. The band at ~1.634 µm greatly increased in depth at Titan temperatures. However, there was no evidence of co-crystal formation.

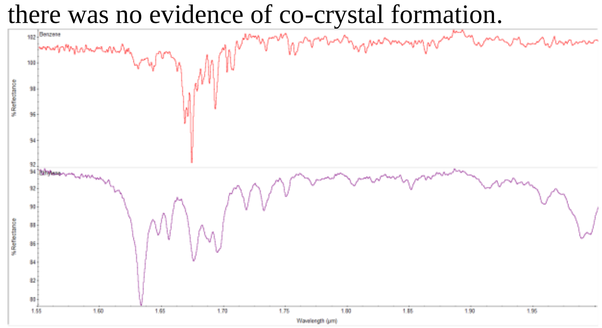

Figure 1: FTIR spectra of pure benzene (top; 162 K) and pure ethylene (bottom; 115 K) for comparison.

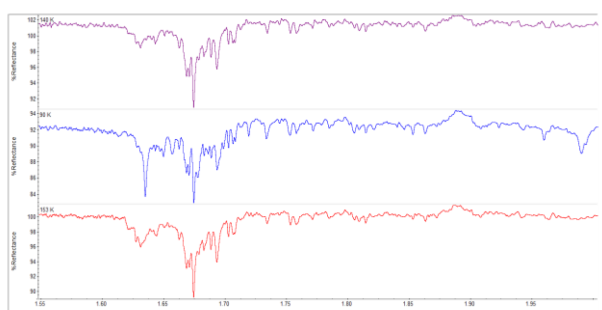

Figure 2: FTIR spectra of benzene and ethylene mixture at different temperatures. Top: Directly after

ethylene was deposited onto the plate with benzene (0 min; 140 K). Middle: Titan-relevant temperature and coldest temperature reached (52 min; 90 K). Bottom: Mixture after it was warmed after reaching Titan temperatures (117 min; 153 K).

Sample Images: Camera positions throughout the TSSC are used to capture images and monitor the experiment. One camera positioned directly above the sample dish provides clear images of the benzene and ethylene (Fig. 3). In each image, solid benzene can be seen as snow-like accumulation. The ethylene is the slightly darker liquid. In one experiment, a "ring" of solid benzene formed and persisted throughout the duration of the experiment. Ethylene did not dissolve this feature, and it did not change as the chamber was cooled or warmed. It is unclear if the ring of benzene formed before the introduction of ethylene, and was merely revealed by it, or if the introduction of ethylene caused the creation of the ring.

Figure 3: Left: Image from inside the TCB, top-down view of sample dish. The accumulation of material is solid benzene. Liquid ethylene (at the bottom of the image) spread outwards as it was poured from the filter. A "ring" of solid benzene is present at the bottom of the image. The liquid ethylene spread out and over this feature, but did not dissolve it. Right: This image was taken five minutes after the image on the left. The ethylene spread further from the ring of benzene as time elapsed, but still did not modify the ring. The temperature at the time of capture for both images was 140 K.

Conclusions: We performed experiments to observe how benzene and ethylene interact under Titan surface conditions using infrared spectroscopy. We observed a change in reflectance as the mixture was cooled and heated, as well as an increase in some band depths as the mixture reached Titan-relevant temperatures. We did not observe any new bands or shifting of bands, leading to the conclusion that contrary to acetylene and ethane, ethylene (liquid) does not form a co-crystal with benzene (solid) at conditions replicating Titan's surface. Perhaps a different ratio of benzene:ethylene would facilitate co-crystal formation. The spectral features of the co-crystal may also be overwhelmed by the ethylene in the spectra and cannot be seen.

This study will add to the body of knowledge surrounding Titan's surface composition and chemical interactions on the surface. These experiments may aid future missions, such as *Dragonfly*. Further experimentation is required with benzene and ethylene at different molecular rations. We plan to perform additional experiments with other Titan-relevant molecules that may interact on the surface and in the lakes. We will also investigate mixtures of more than two compounds, and expand the spectral range of the FTIR.

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