Comparison Study of Surface Energies for Titan Haze Analogs "Tholin".　　　Jialin Li[1], Xinting Yu[2],

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Introduction:　Titan, the largest moon of Saturn, is known for its thick and hazy atmosphere with rich and complex organic materials. Numerous chemical reactions are initiated in Titan's upper atmosphere, resulting in the formation of complex organic aerosol particles that form the thick haze layers. One of the main efforts to better understand the chemistry of the haze is through the synthetic analog materials of Titan's haze, tholins. Several groups have been involved in the production of tholins and analyses of its physical, chemical, and optical properties. Distinct laboratory setups were developed to simulate the various processes that drive photochemistry in Titan's atmosphere (e.g.[1]). The experimental conditions used to produce　Titan aerosol analogs have an impact on their chemical and physical properties, e.g.[2]. Thus, it would be premature to extract the property of one specific laboratory-made tholin and assume it applies to the actual Titan haze analogs. However, only a few studies (e.g. [1,3]) have compared tholin samples made in different laboratories. The study presented here, which aims to characterize a bulk physicochemical property of tholins made by different laboratory groups with distinct laboratory set-ups and experimental conditions, has the potential to reveal common traits between tholins. Traits that are shared by several tholins can be expected to be present in Titan aerosols.

Here we present the results to our comparison study of tholin samples through one specific property: surface energy. The change of free energy when the surface area of a solid is increased by a unit area is defined as surface energy. The free energy change is equivalent to the energy needed to separate two contacting solid surfaces per unit area, determining adhesion and wettability of surfaces and any intervening medium [4]. It has been theorized that the total surface energy be divided into different components, and these individual component values can be informative of the independent intermolecular forces [5]. Surface energy can reveal the fundamental bulk chemical make-up, cohesiveness and wetting properties of a material. Haze particles can act as cloud condensation nuclei for various condensable simple organic molecules to form condensation clouds [6,7], fall to the surface where they partake in fluvial and aeolian processes, and become dune materials and sediments in the polar lakes [8,9]. Surface energy of the Titan hazes has important implications for cloud formation, aerosol-lake interactions, sand transport and dune formation on Titan's surface [10].

Methods: We have measured the surface energy for seven samples from three different laboratories. Two tholin samples were produced in the Planetary Haze Research (PHAZER) chamber at Johns Hopkins University (JHU) from an initial N_2:CH_4 (95:5) gas mixture using two energy sources: an AC glow discharge and a hydrogen UV Lamp [11]. Four tholins samples were produced in the Cosmic Simulation Chamber (COSmIC) at NASA Ames Research Center (ARC) from four different initial gas mixtures: N_2:CH_4 (95:5), N_2:CH_4:C_2H_2 (94.5:5:0.5), Ar:CH_4 (95:5), and Ar:CH_4:C_2H_2 (94.5:5:0.5), using cold plasma discharge as the energy source [12]. One tholin sample was produced in the Photochemical Aerosol Chamber at University of Northern Iowa (UNI) [13] from an initial gas mixture of N_2:CH_4 (95:5) using a deuterium lamp as the energy source.

To measure the surface energy of a tholin sample, a droplet of a test liquid is dispensed onto the sample, using a microsyringe, to form a sessile drop. The test liquids used are HPLC-grade water (FisherChemical™) and diiodomethane (>99%, ACROS Organics™). Each drop process is recorded as video using an goniometer (Osilla). Contact angles are then measured by both the Ossila software and contact angle plugin of the ImageJ software. A comparison test confirmed Osilla and ImageJ return similar contact angle values and can be used interchangeably. The Owens-Wendt-Rabel-Kaelble (OWRK) and Wu analytical methods are then used to estimate the surface energies of each tholin from contact angle measurements. Both assume the surface energy and surface tension can be partitioned into a dispersive component and a polar component. All experiments are performed inside a dry glove box (relative humidity RH <1%) flowed with 99.999% purity dry nitrogen

Results and Discussion: The surface energies of all tholin samples spanned from 45-75 mJ/m² and are listed in Table 1. The surface energies of JHU samples were similar to previous measurements [14]. For the JHU tholin samples, the one produced with plasma (JHU-plasma) has a more substantial polar component

than the one produced with UV (JHU-UV). This can be attributed to the deuterium lamp used to produce JHU-UV, which does not emit the range of photons required to directly dissociate nitrogen in the gas mixture as compounds containing nitrogen are the main contributors to the polar components of the tholins' surface energy. Not having a source of dissociated molecular nitrogen lowers the polar component and therefore the total surface energy of JHU-UV. The UNI tholin sample (UNI-UV) has a similar overall surface energy and surface energy partitioning pattern to JHU-UV. Despite their different experimental conditions, the resemblance can be attributed to their common energy source, the deuterium lamp, and the same initial gas mixing ratio.

Table 1: Derived surface energy of tholin from different methods, all units in mJ/m^2. Both the values of the total surface energy γ_s^{tot} can be divided into the dispersive, γ_s^d, and polar, γ_s^p, components.

Sample	OWRK Method		
	γ_s^d	γ_s^p	γ_s^{tot}
JHU-UV N_2-CH_4	31.5±2.8	16.2±2.8	47.7± 3.4
JHU-Plasma N_2-CH_4	37.4±1.1	35.9±1.5	73.3±1.7
ARC N_2-CH_4	45.7±1.5	20.6±2.2	66.3±2.6
ARC N_2-CH_4-C_2H_2	44.4±0.6	9.0±7.0	53.4±7.0
ARC Ar_2-CH_4	48.3±0.1	0.4±1.2	48.7±1.2
ARC Ar_2-CH_4-C_2H_2	47.5±0.5	1.7±2.8	49.2±2.8
UNI-UV N_2-CH_4	33.9±2.1	19.0±7.4	52.9±7.2

With a cold plasma discharge, dissociation of the molecular nitrogen is possible resulting in for formation of polar compounds in the N_2-based mixtures which participate in the polar component of surface energy, as seen with JHU-plasma. For the tholins produced by plasma chemistry at ARC, although adding heavier precursors in the initial gas mixture results in a more complex chemistry [12], the surface energies are not necessarily higher. When comparing the ARC N_2-CH_4 and ARC N_2-CH_4-C_2H_2 samples, the total and polar components of surface energy of the tholin without acetylene is much higher. Addition of acetylene, a non-polar hydrocarbon precursors, increased the C/N, thus reducing the polar component of surface energy compared to ARC N_2-CH_4. As expected, the ARC Ar-CH_4-C_2H_2 and ARC Ar-CH_4 have polar components close to 0 mJ/m^2. Their initial gas mixtures contained only non-polar constituents, indicating that nitrogen does play a prominent role in the formation of polar components of tholin. For all tholin samples, the dispersive components are relatively high, ranging from about 30-50 mJ/m^2, suggesting that high dispersive components may be a common trait among all tholins. If this is true, haze particles of Titan will likely also have high dispersive components.

The contact angle between ethane and methane, two hydrocarbons present on Titan, and tholins can be estimated from the measured tholin surface energies and the surface tensions and surface energies of ethane and methane. All samples wetted completely with methane and most completely with ethane, suggesting that tholins are likely ideal cloud condensation nuclei (CCN) for heterogeneous nucleation despite their insolubility in these hydrocarbons [1]. Due to the low contact angles between methane and ethane, tholin particles are unlikely to float on the hydrocarbon lakes from capillary forces. The high dispersive components among all tholin samples can lead to similar behaviors towards methane-ethane cloud formation and aerosol-lake interactions. As both methane and ethane have small polar components of surface energy and surface tension, the dispersive components will be the determining factor. The small contact angles can then be attributed to this shared characteristic, implying clouds can likely condensate effectively with haze particles as the CCN and that haze particles that fall to the hydrocarbon lakes would sink to the bottom.

Conclusion and future work: To gain insight into the processes involving the haze on Titan, we compared the surface energy of haze analogs "tholins" made in three laboratories and found that a high dispersive component of surface energy ranging from 30-50 mJ/m^2, is present among all samples.

The estimated contact angle between two hydrocarbons present on Titan, methane and ethane, and the tholins, calculated from the surface energy of tholin, are small. The common trait of high dispersive components suggest that Titan haze particles are likely good cloud condensation nuclei for methane and ethane clouds and sink to the bottom as they sediment. These surface energy measurements can also be connected to other properties of tholins like optical constants, which we plan to investigate in the future.

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