Experimental study on interactions between H atoms and organic haze: Y. Sekine[1,2], H. Imanaka[2], B.N. Khare[2], E.L.O. Bakes[2], C.P. McKay[2], S. Sugita[3], T. Matsui[3] [1]Dept. of Earth and Planetary Sci., Univ. of Tokyo, Bunkyo, Tokyo 113-0033, Japan, [2]NASA Ames Research Center, Moffett Field CA 94025 USA, [3]Dept. of Complexity Sci. and Engineering, Univ. of Tokyo, Kashiwa, Chiba 227-8562, Japan

1. Introduction: In Titan's atmosphere composed of N_2 and CH_4, irradiations of both solar ultraviolet light and charged particles induce active chemical reactions. In the processes of these reactions, a large amount of hydrogen (H) atoms are expected to be formed by dissociation of CH_4 and other hydrocarbons [e.g., 1, 2]. Theoretical models suggest that these active H atoms need to be converted to stable hydrogen molecules (H_2) efficiently to maintain unsaturated hydrocarbons and organic haze in Titan's atmosphere [e.g., 1]. Furthermore, molecular hydrogen is an important greenhouse effect gas in Titan's atmosphere, and small variation in its abundance strongly affects Titan's surface temperature [3]. Thus, the formation of H_2 molecules from H atoms is a key reaction for both the atmospheric chemistry and the surface environment of Titan. Although several numerical calculations have been conducted to investigate the atmospheric chemistry of Titan with hypothesized recombination reactions of H atoms, such as catalytic scheme of C_4H_2 [e.g., 1, 2], it is still unclear what chemical reaction is responsible for the conversion of H atoms to H_2 molecules in Titan's atmosphere.

In this study, we focus on heterogeneous reactions on the surface of Titan haze, which is suggested as one of the conversion process of H into H_2 in Titan's atmosphere [1, 4]. Observations by Voyager and Cassini reveal that Titan's stratosphere contains multiple organic haze layers [e.g., 5]. Some theoretical studies suggest that a H atom in gas phase reacts with another H on the surface of organic haze to form H_2 molecules in Titan's atmosphere [1, 4]. However, there is no experimental investigation on the H_2 formation on the surface of organic solid simulating Titan haze in the literature. Thus, it has been uncertain whether the interaction could occur on the surface of Titan haze.

Here, we conduct laboratory experiments to investigate whether the interactions between H atoms and organic solid simulating Titan haze occur or not. If it occurs, we also investigate the effect of the structure and composition of organic solids on the heterogeneous reaction.

2. Experimental: In order to investigate whether the interactions between H atoms and organic solids occur or not, we first form organic solids from hydrogen -containing gas species, such as CH_4 and C_2H_2, and then irradiate the organic solids with deuterium (D) atoms. If gaseous HD molecules are detected, it will serve as evidence of the interaction between solid and gas phases.

In this study, we produce two types of organic solid simulating Titan haze by cold plasma irradiations inductively coupled with RF power supply (50W). One is formed from N_2-CH_4 gas mixtures (N_2/CH_4=9/1); hereafter we call Titan tholin [6, 7]. The other is formed from pure C_2H_2 gas; hereafter we call acetylene plasma tholin [8]. We also conduct a control experiment without tholin to investigate the effect of adsorbed H_2O on the reaction cell.

The experimental procedure is as follows; first, we form tholin on the wall of a half side of quartz-tubing reaction cell. After evacuating the remaining gas in the cell for 20 hours, D_2 gas is introduced and kept at 6.7 hPa in the closed reaction cell. We slide the RF generator to the other side of the reaction cell to avoid direct irradiation of cold plasma on tholins. Then, we form D atoms by cold plasma in the reaction cell. After a prescribed length of time, a part of the gas in the reaction cell is extracted and analyzed with a residual gas analyzer (RGA) (Stanford Research System, RGA200). The variations in the infrared spectrum of tholin due to D-atom irradiations are measured by FT-IR spectrometer (Nicolet, Nexus 670).

3. Results: Here, we first show the results that indicate the interactions between gas-phase D atoms and tholins. Second, we compare the results of Titan tholin and acetylene plasma tholin.

Interactions between D atoms and organic tholins: Figure 1 shows the time evolutions of the partial pressure of D_2 and the RGA ion current value for mass number 3 (HD). Every experiment is conducted twice, and the mean values are given. Both the partial pressure of D_2 gas decreases and that of HD gas increases as functions of time in all three cases. However, both the formation of HD gas and the consumption of D_2 gas proceed more efficiently in the experiments with tholins than those without tholin on the reaction cell. The result of the control experiment without tholin indicates that the amount of HD gas formed from H_2O is less than 50 % of total amount of HD gas formed in the experiment with tholins. The larger increases in HD gas in the experiment with tholins indicate that HD gas is formed through the interactions between D atoms and organic tholins.

The IR measurements of tholins indicate that Titan tholin contains C-H, N-H, C=C, C=N, and C≡N bands, and that acetylene plasma tholin contains C-H, C=C, and ≡C-H bands. Figure 2 compares the IR transmittances of acetylene plasma tholin before and after 30-minute-long

D atom irradiation. We can see that significant intensities of the C-D stretching bands around 2050 – 2250 cm^{-1} appear after D atom irradiation. This result indicates that some fractions of D atom in the gas phase are embedded in tholin.

Our experimental results of the gas phase (Fig. 1) and the solid phase (Fig. 2) indicate that the HD gas formation occurs as a result of the interactions between D atoms and organic tholins.

The effect of structure and composition of tholins: In the experiment of D atom irradiation on tholins, we also observe the significant increases in RGA ion current values for mass numbers of 19 (CHD_3) and 20 (CD_4). Figure 3 shows the time evolution of the ion current value for mass number of 19 normalized by that for 18. Our experimental result indicates that D atoms extract carbon in tholins and form CHD_3.

Next, we compare the results of Titan tholin and acetylene tholin concerning the gas product formed by the heterogeneous reaction. Our results in Figs. 1 and 3 show that Titan tholin forms HD efficiently, while acetylene plasma tholin forms CHD_3 efficiently. This result indicates that the structure and composition of tholin affect the gas products formed through heterogeneous reactions.

4. Discussions & Conclusions: Our results indicate that the heterogeneous interactions occur on the surface of organic solid simulating Titan haze. These experimental results strongly suggest that photochemically dissociated H atoms react with organic haze to form H_2 molecules in Titan's atmosphere. This reaction may result in low concentration of reactive H atoms and consequently high concentration of unsaturated hydrocarbons in Titan's stratosphere.

Our results also indicate that the structure and composition of tholin affect the gas species formed by the heterogeneous reaction. For instance, Titan tholin, formed from N_2-CH_4 gas mixtures, produces H_2 efficiently, while acetylene plasma tholin, formed from C_2H_2 gas, produces CH_4 efficiently as a result of the interactions with H atoms. The pyrolysis GCMS analysis by Huygens probe may provide the information about the structure and composition of Titan haze. These observational data could also be important in investigating the heterogeneous reaction in Titan's atmosphere, especially the production of H_2 and CH_4.

Refferences: [1] Yung Y.L. et al., *APJ Supp.*, 55, 1984, [2] Lebonnois S. et al., *Icarus*, 161, 2003, [3] McKay C.P. et al., *Science*, 253, 1991, [4] Bakes E.L.O. et al., *Icarus.*, 161, 2003, [5] Smith B.A. et al. *Science*, 212, 1981 [6] Khare B.N. et al., *Icarus*, 60, 1984 [7] Imanaka H. et al., *Icarus.* 168, 2004 [8] Bar-Nun A., *JGR*,. 93 1988

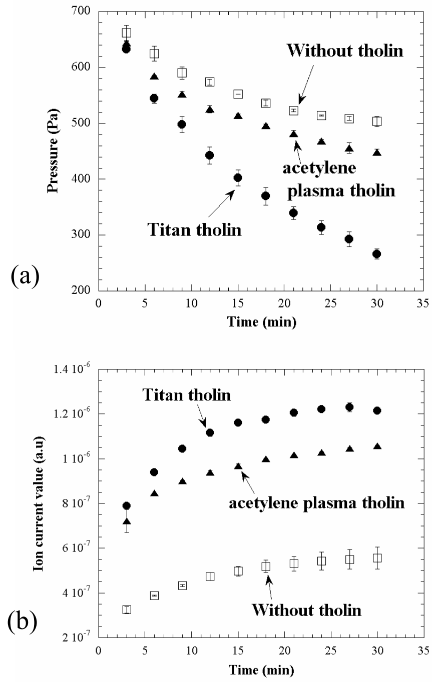

Figure 1. Time evolutions of partial pressure of D_2 (a) and the RGA ion current value for mass number 3 (HD) (b). The solid circles and triangles indicate our experimental results with Titan tholin and acetylene plasma tholin on the reaction cell, respectively. The open squares indicate the results without tholin.

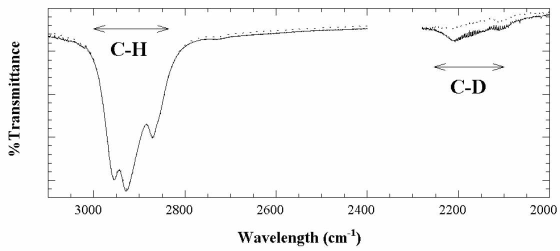

Figure 2. IR transmittance of acetylene plasma tholin before (dotted line) and after 30-minute-long after D atom irradiation (solid line) at 2000 – 3100 cm^{-1}.

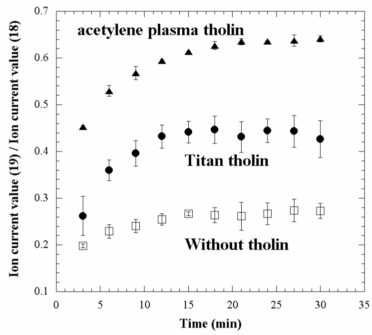

Figure 3. Time evolution of the RGA ion current value for mass number of 19 normalized by that of 18. The solid circles, solid triangles, and open squares indicate our experimental results with Titan tholin and acetylene plasma tholin and without tholin on the reaction cell, respectively.