

**Stable Isotope Fractionation in Titan Aerosol Formation.** M. S. Ugelow<sup>1,2</sup>, M. G. Trainer<sup>3</sup>, S. T. Wieman<sup>3,4</sup>, J. C. Stern<sup>3</sup>, M. C. Roach<sup>5</sup>, and J. A. Sebree<sup>5</sup>, <sup>1</sup>Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, 80309, USA, [Melissa.Ugelow@colorado.edu](mailto:Melissa.Ugelow@colorado.edu); <sup>2</sup>Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, 80309, USA; <sup>3</sup>Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA; <sup>4</sup>CRESST II, University of Maryland, Baltimore County, Baltimore, MD 21250, USA; <sup>5</sup>Department of Chemistry and Biochemistry, University of Northern Iowa, Cedar Falls, IA 50614, USA

**Introduction:** Stable isotope ratio measurements are a powerful tool used to understand both ancient and modern planetary processes. Instruments on the Cassini-Huygens spacecraft along with ground-based observations have measured several isotope pairs, including  $^{13}\text{C}/^{12}\text{C}$  and  $^{15}\text{N}/^{14}\text{N}$ , in Titan's atmosphere [1]. This includes isotopic measurements of the major atmospheric species,  $\text{CH}_4$  and  $\text{N}_2$ , along with  $\text{HCN}$ ,  $\text{HC}_3\text{N}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$  and  $\text{C}_4\text{H}_2$  [2-13]. However, the isotopic fractionation of Titan's organic aerosol has not conclusively been measured and therefore the effect of aerosol formation as an isotopic fractionation pathway in Titan's atmosphere has not been considered.

Laboratory studies have measured the carbon and/or nitrogen isotopic fractionation of Titan aerosol analogs [14-18]. [18] found that the carbon fractionation of photochemical organic aerosol analogs are more enriched in  $^{13}\text{C}$ . This enrichment in the aerosol analogs is opposite of what is predicted for photochemical products by the kinetic isotope effect. Additionally, both [16] and [18] found that the nitrogen fractionation in the organic aerosol analogs are opposite of what is observed in Titan's atmospheric  $\text{N}_2$  and  $\text{HCN}$ , with the aerosol analogs being a light nitrogen sink.

Here we monitor the gas phase during photochemical aerosol analog production as a function of reaction time. In a recirculation experiment, the isotopic fractionation of carbon within the gas-phase products is measured as the  $\text{CH}_4$  reservoir is depleted. This allows us to monitor the isotopic fractionation pathway during photochemical aerosol analog formation.

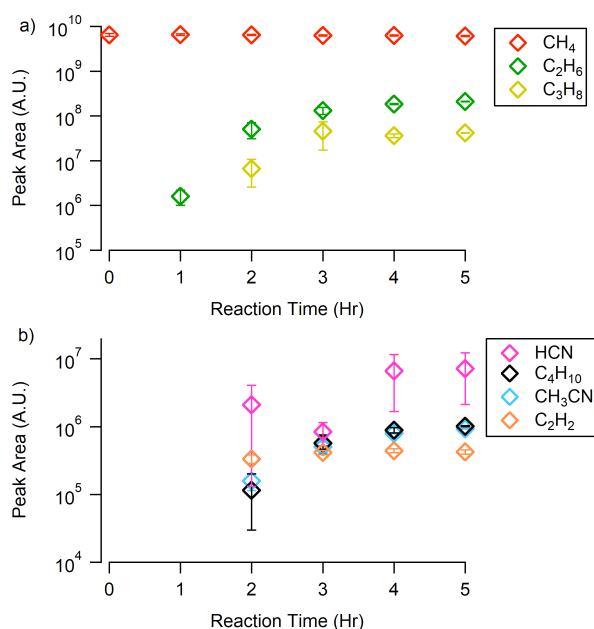
### Experimental Methods:

**Titan aerosol analog formation.** Titan aerosol analogs are produced in a new recirculating photochemical flow reactor using gas mixtures of 5%  $\text{CH}_4$  in  $\text{N}_2$ . The gas mixtures are exposed to a deuterium lamp that outputs between 115 and 400 nm. Unlike previous studies [18-20], the flow reactor is a closed system that recirculates unreacted  $\text{CH}_4$  and  $\text{N}_2$  along with secondary gas phase products. A gas sampling port is attached downstream of the deuterium lamp.

**Instrumentation.** The gas phase species are extracted from the gas sampling port using gas-tight syringes. The consumption of  $\text{CH}_4$  and the presence of secondary gas phase products are monitored by a Thermo

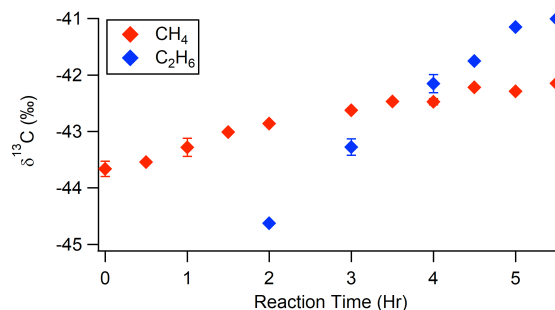
Scientific Trace 1310 Gas Chromatograph with a Restek Rt-Q-BOND PLOT column coupled to a Thermo Scientific ISQ QD single quadrupole mass spectrometer (GC-MS). The  $\delta^{13}\text{C}$  measurements are made on a Thermo Scientific Trace Ultra GC Isolink with a Carboxen 1006 PLOT column (Supelco) coupled to a Thermo Scientific Delta V isotope ratio mass spectrometer (IRMS).

**Results and Discussion:** Figure 1 shows the gas phase species measured during aerosol analog formation characterized by the GC-MS. As  $\text{CH}_4$  is consumed with the progression of the aerosol formation reaction, smaller chained alkanes and nitriles are produced. By the fourth to fifth hour of the aerosol formation reaction, the measured gas phase species reach a steady-state. Additionally, the gas species in-



**Figure 1.** The gas phase species measured by GC-MS during aerosol formation that are produced in large enough concentrations to obtain an isotopic fractionation measurement (a) and the other gas phase species produced that are below the detection limit of the IRMS (b). Preliminary data with error bars that represent the  $1\sigma$  standard deviation of the peak area reproducibility

cluded in Figure 1a are the species that are produced (or remain) at sufficient abundances to be able to obtain isotopic fractionation measurements. Due to low signal-to-noise, however, we have thus far been unable to measure the isotopic composition of the evolved propane. The gas species in Figure 1b have been observed to be too low in concentration with the current experimental protocol to be measurable by IRMS.



**Figure 2.** Carbon isotopic fractionation (VPDB) of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ .

The carbon isotopic fractionation has been measured for  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  and is shown in Figure 2. The reaction time of 0 hours corresponds to the unreacted, background-level carbon isotopic fractionation of the source  $\text{CH}_4$ . Given that photochemical aerosol analogs are enriched in  $^{13}\text{C}$  relative to the starting mixture, we expect the recirculating gas mixture to become isotopically depleted over time. However, our observations show the opposite result; as the reaction progresses, both  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  become enriched in  $^{13}\text{C}$ , as well.

Moreover, as expected, the  $\text{C}_2\text{H}_6$  is originally isotopically depleted relative to the gas mixture  $\text{CH}_4$  that it originates from. However, the enrichment of  $^{13}\text{C}$  in  $\text{C}_2\text{H}_6$  occurs faster than that of  $\text{CH}_4$ . This rapid enrichment to an isotopic composition heavier than the source  $\text{CH}_4$  potentially points to a different or additional reaction pathway(s) either producing or consuming the  $\text{CH}_4$ .

The light carbon sink in the recirculating photochemical flow reactor remains unknown. Longer running experiments and accurate measurements of propane may better elucidate the isotopic pathways. Additionally, different GC methods and columns that better resolve the additional gas species produced during aerosol analog formation can enhance our ability to measure the carbon isotopic fractionations of these species and potentially uncover the identity of the light carbon sink(s).

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