Effect of Titan-like aerosol formation on $\delta^{13}$C of major gas phase products. S.T. Wieman$^{1,2,3}$, M.S. Ugelow$^{4,5}$, V. Da Poian$^{6,2,3}$, M.C. Roach$^{7}$, J.C. Stern$^{2}$, M.G. Trainer$^{3}$. $^1$Center for Space Sciences and Technology, University of Maryland, Baltimore County, Baltimore, MD 21250 $^2$Planetary Environments Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771 $^3$Center for Research and Exploration in Space Science and Technology, NASA Goddard Space Flight Center, Greenbelt, MD 20771 $^4$Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771 $^5$University Space Research Association, Columbia, MD 21046 $^6$Southeastern Universities Research Association, Washington, DC 20005 $^7$Chemistry Department, Colorado State University, Fort Collins, CO 80523

**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 in Titan’s atmosphere, including $^{13}$C/$^{12}$C and $^{15}$N/$^{14}$N [1]. This includes isotopic measurements of the major atmospheric species, CH$_4$ and N$_2$, along with HCN, HC$_3$N, C$_2$H$_2$, C$_3$H$_4$ and C$_6$H$_2$ [2-13]. Measurements of Titan’s methane have been unable to differentiate its carbon isotopic composition from the protosolar value. This lack of fractionation may indicate that the methane in Titan’s atmosphere is either relatively young or regenerated from within the crust. While most atmospheric processes that influence fractionation are well understood, the effect of photochemical aerosol formation on the fractionation of carbon isotopes between different gas phase species remains largely unknown.

Laboratory studies have measured the carbon and/or nitrogen isotopic fractionation of Titan aerosol analogs [14-17]. Sebree et al. [17] found that the carbon fractionation of photochemical organic aerosol analogs are enriched in $^{13}$C relative to the reactant methane. This enrichment in the aerosol analogs is in opposition to the predicted kinetic isotope effect on photochemical products. Additionally, both [16] and [17] found that the nitrogen fractionation in the organic aerosol analogs are contrary to what is observed in Titan’s atmospheric N$_2$ and HCN, with the aerosol analogs being a light nitrogen sink.

Here, we measure compound-specific isotope ratios and abundances of gas phase species during photochemical aerosol analog production over time. In a recirculating experiment, the isotopic fractionation of carbon within the gas phase products is measured as the CH$_4$ reservoir is depleted. This allows us to monitor the isotopic fractionation pathway during photochemical aerosol analog formation. Adaptations to our experimental setup have been made to drive the reaction towards more products by reducing reaction-terminating hydrogen in the photochemical chamber. These changes have enabled us to measure the isotopic ratios of methane, ethane, and propane.

**Experimental Methods:**

Titan aerosol analog formation. Titan aerosol analogs are produced in a recirculating photochemical flow reactor using gas mixtures of 5% CH$_4$ in N$_2$. The gas mixtures are exposed to a deuterium continuum lamp that outputs between 115 and 400 nm. Unlike previous studies [17-19], the flow reactor is a closed system that recirculates unreacted CH$_4$ and N$_2$ along with secondary gas phase products. A gas sampling port is attached downstream of the deuterium lamp. The removal of generated hydrogen is achieved by the addition of a heated palladium membrane to the recirculating system. The hydrogen is then pumped away while the other gas phase species are unaffected.

**Instrumentation.** The gas phase species are extracted from the gas sampling port using gas-tight syringes. The consumption of 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 $\delta^{13}$C measurements are made on a Thermo Scientific Trace Ultra GC Isolink with a Restek Rt-Q-BOND PLOT column coupled to a Thermo Scientific Delta V isotope ratio mass spectrometer (IRMS).

**Results and Discussion:** Figure 1 shows the major gas phase species measured in the recirculating system, CH$_4$, C$_2$H$_6$, and C$_3$H$_8$, during 24 hours of aerosol formation as characterized on the GC-MS. As CH$_4$ is consumed, longer-chain hydrocarbons are produced.

![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.](image)

While we had previously observed a peak in secondary product production around hour 5 [20], hydrogen removal increases the concentration of secondary
products produced by about 50% and shifts peak production back to hour 12. Previously, we had observed secondary gas products dropping in abundance after their peak. With the removal of hydrogen, however, products instead plateau or slightly increase after the hour 12 peak. In our improved instrumental setup, ethane and propane are created in sufficient quantities to measure their $\delta^{13}$C but other products remain too low for isotopic measurements.

The carbon isotopic fractionation has been measured for CH$_4$, C$_2$H$_6$, and C$_3$H$_8$ and is shown in Figure 2. The $\delta^{13}$C at time point 0 is the carbon isotopic ratio of the starting CH$_4$. Given that photochemical aerosol analogs are enriched in $^{13}$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 all three species become enriched in $^{13}$C over time. Over the first several hours, methane becomes isotopically heavier. By hour 10, methane’s carbon isotope ratio plateaus at 1.3 $\pm$ 0.3% above its starting value and thereafter remains constant.

![Figure 2](image)

**Figure 2.** Carbon isotopic fractionation (VPDB) of CH$_4$, C$_2$H$_6$, and C$_3$H$_8$.

C$_2$H$_6$ and C$_3$H$_8$ are both isotopically depleted relative to the starting CH$_4$. When first measured at hour 2, C$_2$H$_6$ is 7% lighter than the starting methane, but it rapidly enriches over the span of the experiment. After 21 hours, C$_2$H$_6$ becomes heavier than the original starting methane, but it remains lighter than the methane present at the same time point. Propane behaves similar to ethane, as it is originally 9.5% lighter than the starting methane and also rapidly enriches. However, propane enriches more slowly than ethane and never approaches the isotopic ratio of the starting methane.

The removal of hydrogen from our system results in lighter carbon isotope compositions of ethane and propane compared with our prior experiments. In our past work, ethane grew isotopically heavier than the starting methane by the third hour and grew heavier than the simultaneously occurring methane by the fifth hour. In these new experiments, ethane only surpasses the isotope ratio of the starting methane in hour 21 and always remains lighter than the methane in the system. This change in carbon fractionation between species provides insight into what photochemical reactions may dominate on Titan, where hydrogen can be lost to space instead of dominantly participating in photochemical reactions, as observed in our previous experiments without hydrogen removal.

As the majority of gaseous species remain below the detection limit on the IRMS, the full distribution of carbon in our recirculating photochemical flow reactor remains unknown. Incorporation of a trapping substance and development of subsequent desorption methods will hopefully provide sufficient quantities of minor species for isotopic determination. Of particular interest are HCN and CH$_3$CN, as these compounds can help elucidate the additional influence of nitrogen on carbon isotopic fractionation in Titan’s atmosphere.

**References:**


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