

# Titan Aerosol Formation as a Sink for Stable Carbon and Nitrogen Isotopes

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## Abstract

Stable isotope ratios of major elements can be used to infer much about local- and global-scale processes on a planet. On Titan, aerosol production is a significant sink of carbon and nitrogen in the atmosphere, and isotopic fractionation of these elements may be introduced during the advanced organic chemistry that leads to the condensed phase products. Here we report on the isotopic composition of analogs of Titan's organic aerosol generated in the laboratory via photochemistry of CH<sub>4</sub> and N<sub>2</sub> gas mixtures.

## 1. Introduction

Several stable isotope pairs, including <sup>12</sup>C/<sup>13</sup>C and <sup>14</sup>N/<sup>15</sup>N, have been measured *in situ* or probed spectroscopically by Cassini-borne instruments, space telescopes, or through ground-based observations. However, the effect of a potentially critical pathway for isotopic fractionation – organic aerosol formation and subsequent deposition onto the surface of Titan – has not been considered due to insufficient data regarding fractionation during aerosol formation. To better understand the nature of this process, we have measured the isotopic fractionation associated with the formation of Titan aerosol analogs via far-UV irradiation of several methane (CH<sub>4</sub>) and nitrogen (N<sub>2</sub>) mixtures.

## 2. Experimental Methods

The Titan aerosol analogs used in this study were generated in a photochemical flow reactor (far UV: 115 - 400 nm), described previously [1]. Gas mixtures were prepared by the addition of methane into a mixing chamber with N<sub>2</sub> as a balance gas, with concentrations ranging 0.005 - 1.5% CH<sub>4</sub> in N<sub>2</sub>. Previous work indicated chemical composition of the aerosol products should not vary substantially across this concentration range, though production rates do vary by more than 2 orders of magnitude [2].

Aerosols formed in the chamber were collected on a glass fiber filter and analyzed for bulk δ<sup>13</sup>C and δ<sup>15</sup>N with a Costech Elemental Analyzer (EA) - Thermo Scientific Delta V isotope ratio mass spectrometer (IRMS). Several filter segments were measured for each sample of collected aerosol. Measurement of the δ<sup>13</sup>C in CH<sub>4</sub> in the starting gas mixture was performed using gas injection on a Thermo Trace Ultra GC Isolink with Carboxen 1006 PLOT column coupled to the IRMS. The δ<sup>15</sup>N of the N<sub>2</sub> balance gas was measured by direct injection into a gas/liquid injection port on the EA coupled to the IRMS.

We report the Δ<sup>13</sup>C of the aerosol product, defined as  $\Delta^{13}\text{C} = \delta^{13}\text{C}_{\text{products}} - \delta^{13}\text{C}_{\text{reactants}}$ , to describe the isotopic composition of the products relative to starting gas composition, where

$$\delta(\text{‰}) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \cdot 1000 \quad (1)$$

## 3. Results and Discussion

An extensive report on the results of this study and discussion of the implications has been reported in a recent publication by Sebree et al [3]. A summary is provided here.

Our results show that the direction of carbon isotope fractionation during aerosol formation is in contrast to the expected result if the source of the fractionation is a kinetic isotope effect (Fig. 1). Explanations for the source of the observed fractionation include: (1) aerosol formation pathways dependent on initial gas phase products with positive δ<sup>13</sup>C; (2) non-kinetic fractionation during photolysis reactions, such as the processes that cause “mass-independent fractionation” in S and O isotopes in Earth’s atmosphere; or (3) some combination of these effects.

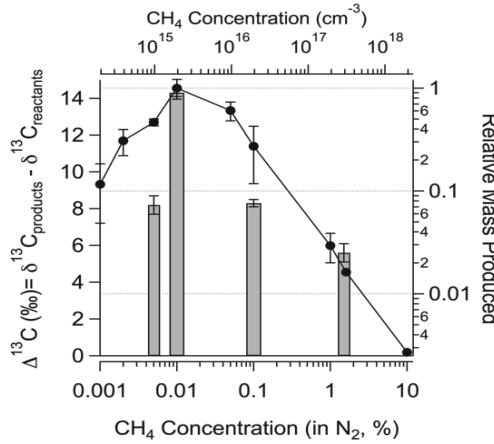


Figure 1: The isotopic composition of carbon in the photochemical aerosol products relative to the reactant gas shows enrichment in <sup>13</sup>C (bars, left axis), with a trend similar to the aerosol mass production (circles, right axis) [2].

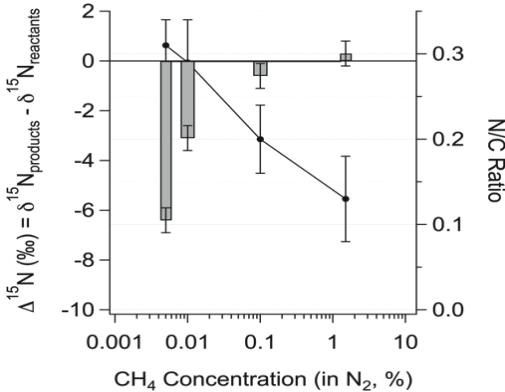


Figure 2: The isotopic composition of nitrogen in the photochemical aerosol products relative to reactant gas shows enrichment in <sup>14</sup>N (bars, left axis), increasing with a bulk increase in the N/C ratio (circles, right axis) of the aerosol products.

Our negative  $\Delta^{15}\text{N}$  value is the opposite of what is observed for HCN and  $\text{N}_2$  in Titan measurements (Fig. 2). Our UV source does not cover the relevant wavelength range for producing the fractionation directly from  $\text{N}_2$ , but rather shows that the previously observed incorporation of nitrogen into aerosols via lower energy pathways [4]. The direction of the fractionation is the same as that observed by Kuga et al. [5] from plasma experiments, with a slightly lower magnitude.

## 4. Summary and Conclusions

In this study, we have analyzed the carbon and nitrogen fractionation of a series of photochemically generated aerosols produced from several mixtures of  $\text{CH}_4$  and  $\text{N}_2$  [3]. The resulting aerosols were enriched in <sup>13</sup>C and <sup>14</sup>N. When put in the context of Titan's atmosphere, photochemically-produced aerosols may form a sink for <sup>13</sup>C, possibly resulting from secondary reaction pathways that do not depend on the KIE. The enrichment of <sup>14</sup>N in the aerosols, if present on Titan, could contribute to an overall enrichment in <sup>15</sup>N in Titan's atmosphere as the condensed particles settle out.

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