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^{13}C and ^{15}N fractionation of CH_4/N_2 mixtures during photochemical aerosol formation: Relevance to Titan

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Abstract

The ratios of the stable isotopes that comprise each chemical species in Titan's atmosphere provide critical information towards understanding the processes taking place within its modern and ancient atmosphere. Several stable isotope pairs, including $^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$, have been measured *in situ* or probed spectroscopically by Cassini-borne instruments, space telescopes, or through ground-based observations. Current attempts to model the observed isotope ratios incorporate fractionation resulting from atmospheric diffusion, hydrodynamic escape, and primary photochemical processes. 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 conducted a laboratory study to measure the isotopic fractionation associated with the formation of Titan aerosol analogs, commonly referred to as 'tholins', via far-UV irradiation of several methane (CH_4) and dinitrogen (N_2) mixtures. Analysis of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic signatures of the photochemical aerosol products using an isotope ratio mass spectrometer (IRMS) show that fractionation direction and magnitude are dependent on the initial bulk composition of the gas mixture. In general, the aerosols showed enrichment in ^{13}C and ^{14}N , and the observed fractionation trends can provide insight into the chemical mechanisms controlling photochemical aerosol formation.

Keywords

Titan, atmosphere; Atmospheres, chemistry; Atmospheres, composition

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1. Introduction

A comprehensive understanding of the chemical and physical processes taking place in Titan's atmosphere, both past and present, not only requires consideration of the compounds present in the atmosphere, but also the ratios of the stable isotopes that make up the individual species. Observations from several of the instruments onboard the Cassini spacecraft along with Earth-based observations have allowed for the measurement of several stable, non-radiogenic, isotope pairs including D/H, $^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$ and $^{16}\text{O}/^{18}\text{O}$ (Bézard et al., 2014). Of particular interest are the $^{12}\text{C}/^{13}\text{C}$ ratio of Titan's atmospheric methane and the $^{14}\text{N}/^{15}\text{N}$ in molecular nitrogen. The value of the carbon isotope ratio can be used in determining the age and history of the methane in the atmosphere (Mandt et al., 2012; Nixon et al., 2012), while the nitrogen isotope ratio is important for understanding the origin of nitrogen on Titan (Mandt et al., 2014).

Recent measurements from Titan indicate that the $^{12}\text{C}/^{13}\text{C}$ ratio in CH_4 is similar to that found in carbonaceous chondrites ($^{12}\text{C}/^{13}\text{C} \sim 89$) (Alexander et al., 2007; Martins et al., 2007), indicating either that the methane is relatively young and has not evolved away from the protosolar ratio, or that it has been recently replenished, possibly through cryovolcanism (Mandt et al., 2009). Measurements of other carbon-bearing species do not show further isotopic fractionation within the sensitivity of current mission instruments, as summarized in Fig. 1. This apparent lack of carbon isotope fractionation during processing in the Titanian atmosphere is contrary to that expected for a chemically active atmosphere subjected to escape processes (Mandt et al., 2009, 2012).

In contrast, the $^{14}\text{N}/^{15}\text{N}$ ratio does show considerable fractionation between different species (Table 1). The $^{14}\text{N}/^{15}\text{N}$ ratio has been measured for both molecular nitrogen (N_2) for and hydrogen cyanide (HCN), with HCN showing a near 3-fold enrichment in ^{15}N over the bulk N_2 (Vinatier et al., 2007). Both are significantly enriched in ^{15}N compared to the protosolar value for N_2 , but the $^{14}\text{N}/^{15}\text{N}$ in N_2 is within the range measured for the protosolar value of NH_3 based on comet measurements (Shinnaka et al., 2014; Rousselot et al., 2014). The similarity between comets and Titan, the depletion of primordial noble gases relative to nitrogen (Niemann et al., 2005, 2010), along with limits to the amount of fractionation possible over time (Mandt et al., 2014), suggests that Titan's nitrogen originated as NH_3 from the protosolar nebula.

While several models have been developed to account for the observed isotope ratios, there are still gaps in our understanding of the entire system, for which laboratory data are needed. Current models assume fractionation occurs through three main processes: atmospheric diffusion, various escape processes, and primary chemical reactions (Mandt et al., 2009, 2012; Hunten, 1982; Liang et al., 2007; Nixon et al., 2012). Atmospheric diffusion causes isotope fractionation with altitude, where lighter isotopes diffuse more effectively into the upper atmosphere, while heavier isotopes remain closer to the surface (Hunten, 1982). Coupled with escape, the preferential loss of lighter isotopes from the atmosphere leads to an increase in the fraction of heavy isotopes in the bulk atmosphere (Hunten, 1982; Mandt et al., 2012).

Chemical processing is the least understood fractionation pathway. Photochemical models (e.g. Wilson and Atreya, 2009) identify five processes for methane depletion and creation. Assuming that the initial photochemical reactions undergo a kinetic isotope effect (KIE), the lighter isotopes react slightly faster, and therefore more often ($\sim 1.004:1$ for ^{12}C versus ^{13}C). This causes products to be enriched in lighter isotopes and residual reactant to be enriched in heavier isotopes (Mandt et al., 2012; Nixon et al., 2012). For example, the conversion of CH_4 to methyl radical (CH_3) by ethynyl radical – the largest single source of methane loss in Titan's atmosphere (Wilson and Atreya, 2009) – proceeds such that the rate of loss of $^{12}\text{CH}_4$ versus $^{13}\text{CH}_4$ only differ by a few percent [$k(^{12}\text{CH}_4)/k(^{13}\text{CH}_4) \approx 1.01\text{--}1.08$]. This should cause a slight enrichment in $^{13}\text{CH}_4$ in the atmosphere over geologic time scales (>50 Myr), but uncertainties in the loss rates can increase or decrease the time scale by as much as a factor of four (Nixon et al., 2012).

A limitation of these models is their inability to account for the isotope reaction preferences in all of the reactions on the pathway to aerosol formation. This is due to both the complex nature of aerosol formation chemistry, as well as the lack of laboratory measurements of isotope fractionation in the reactions leading up to aerosol formation. Yet the aerosol phase can be an important reservoir for carbon and hydrogen, and is a non-negligible reservoir for nitrogen atoms. Therefore, the lack of accounting of isotopic fractionation during aerosol formation pathways could lead to deficiencies in our understanding of isotopic cycling in the Titan atmosphere. At present, estimates of the haze column production rates from photochemical models vary widely from ~ 3 to $12 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ (Krasnopolsky, 2009; Wilson and Atreya, 2009; Vuitton et al., 2012), or from $\sim 20\%$ to 200% of the ethane production rates in the same models. Therefore, the haze layer is one of – and possibly the most – important carbon sinks of Titan's methane destruction, and understanding the fractionation mechanisms in haze production is critical to interpretation of the isotopic ratios (especially $^{12}\text{C}/^{13}\text{C}$) measured in the gas phase (methane and ethane). If the chemistry leading to aerosol formation were sensitive to isotope effects, then aerosol particles, which can settle out to the surface, would also preferentially remove certain isotopes. However, this cannot be properly evaluated with the current scarcity of isotopic fractionation data from laboratory studies.

To date, there have been no studies of isotope fractionation in Titan aerosol analogs formed solely from UV irradiation, which is the primary energy source in Titan's atmosphere that leads to aerosol formation (Lavvas et al., 2011). There have been a few laboratory studies on isotope fractionation in aerosols produced from CH_4 . Chang et al. (1983) used both a spark discharge and 124 nm photolysis on various mixtures (pure CH_4 , $\text{CH}_4\text{--NH}_3\text{--H}_2\text{O}$ and $\text{CH}_4\text{--N}_2\text{--H}_2\text{O}$) to produce aerosols. The resulting products, while not strictly relevant to Titan, all showed enrichment in ^{12}C . In a later Titan-focused laboratory study by Nguyen et al. (2007, 2008), mixtures of 2% CH_4 in N_2 were initiated with cold plasmas yielding inconclusive results: products were enriched in either ^{13}C or ^{12}C , depending on the plasma source. The scope of this study was narrow with no follow-on work to clarify the carbon fractionation inconsistencies.

In a recent study by Kuga et al. (2014), mixtures with CH_4 concentrations ranging from 1% to 10% in N_2 were flowed through a plasma discharge that initiated the formation of aerosol

products. The resultant aerosols show depletion in ^{15}N of around -20‰ relative to the initial N_2 gas. While this is small compared to the $\sim 4300\text{‰}$ fractionation observed between HCN and N_2 in Titan's atmosphere, it does suggest aerosols generated via electron impact with high rates of nitrogen dissociation are a sink for ^{14}N . The plasma results were broadly consistent with isotopic fractionation driven by kinetic effects and aerosol formation resulting from polymerization of species such as HCN and/or CH_2NH . In this and other plasma-based studies there is UV light produced in the plasma. However the photon densities are not well quantified and are likely orders of magnitude lower than the energetic electrons, and therefore not a dominant source for the chemistry. Owing to the nature of the reactions within the plasma reactor and equal electron dissociation cross-sections for the N_2 isotopologues, results of this study may not reflect isotopic fractionation that occurs with photochemical aerosol formation, which accounts for the bulk of the daytime chemistry. Further, carbon isotope measurements were not reported.

Here, we present the first isotope-focused study of photochemically generated aerosols that looks at both nitrogen and carbon isotopes. In this work, we augment the plasma fractionation data with laboratory measurements of fractionation during photochemical aerosol formation. Here we report the $^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$ fractionations, as well as the N/C ratio, of aerosols formed from CH_4/N_2 gas mixtures.

2. Experimental details

The Titan aerosol analogs used in this study were generated in a photochemical flow reactor that has been previously described, most recently in Sebree et al. (2014). Gas mixtures were prepared by the addition of methane into a mixing chamber with N_2 as a balance gas. Gas reagents (Airgas, Inc.) had minimum purities of 99.99 and 99.999% for CH_4 and N_2 respectively. Prepared gas mixtures were then flowed into a $\sim 300\text{ cm}^3$ glass reaction cell at a rate of 100 sccm (standard cubic centimeters per minute). The cell was maintained at room temperature and a pressure of 600 Torr. While in the reaction cell, the mixture underwent UV-irradiation (range 115–400 nm) by a water-cooled deuterium lamp (Hamamatsu, L1835), and the resulting aerosols were collected downstream on a quartz fiber filter.

Titan CH_4 concentrations range from $\sim 2\%$ in the very upper atmosphere (Waite et al., 2005), to as low as 1% in the stratosphere (Lellouch et al., 2014), and close to 6% at the surface (Niemann et al., 2010). For our starting gas compositions, we used mixtures of 0.005%, 0.01%, 0.1% and 1.5% CH_4 in N_2 . Our experimental concentrations were chosen based on a previous study (Trainer et al., 2006), which showed that the chemical composition of the aerosol products did not vary substantially across this concentration range, while the production rates did vary by more than 2 orders of magnitude. This allowed us to maximize the quantity of aerosol product while minimizing the amount of collection time, which was already on the order of days. In the previous work aerosol production was observed to occur in two reaction regimes, demarcated by the concentration at which this cell was optically thick at the Lyman- α (121.6 nm) wavelength at the experimental pressure – approximately 0.02% CH_4 in N_2 . At $[\text{CH}_4] < 0.02\%$ the reactions were CH_4 -limited, and at conditions of $[\text{CH}_4] > 0.02\%$ they were photon-limited. By studying the isotopic composition of products

from starting conditions that straddle both reaction regimes, we are able to probe different controlling factors for observed fractionations.

In order to minimize contamination, the aerosols formed in the chamber were collected on a glass fiber filter (Millipore/AQFA 47 mm) in a collection chamber. This chamber was then isolated and removed from the line while still under vacuum and placed in a glove box that was flushed with argon. While in the glove box, the sample chamber was opened, the filter with the aerosols was removed, segmented, and each filter portion was packed into tin capsules. These capsules were loaded into the autosampler of a Costech Elemental Analyzer (EA) for bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis via a Thermo Scientific Delta V isotope ratio mass spectrometer (IRMS). In the EA the loaded aerosol samples are flash-combusted at 980 °C under a flow of helium, quantitatively converting all carbon to CO_2 and nitrogen to N_2O . A reduction column removed excess oxygen and reduced oxidized nitrogen compounds to N_2 , and a GC column separates CO_2 and N_2 prior to optional He dilution and delivery to the IRMS. Several filter segments were measured for each sample of collected aerosol, and a minimum of four to eight unique samples (different aerosol “batches”) were run for each mixture to check reproducibility. The uncertainties reported in the results are the standard deviation of the mean value for each concentration.

Carbon and nitrogen stable isotope values are reported in standard 5 notation in per mil (‰) as defined by:

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

where R_{sample} is the ratio of the heavy to light isotope in a sample (here, $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$), and R_{standard} is this ratio in a standard. The $\delta^{13}\text{C}$ is reported relative to the international standard Vienna Pee Dee Belemnite (V-PDB; $R_{\text{standard}} = 0.0112594$), and $\delta^{15}\text{N}$ is reported relative to N_2 in Earth’s atmosphere ($R_{\text{standard}} = 0.003676$) (Lodders and Fegley, 1998).

Reported $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were calibrated against a commercial alanine standard of known isotopic composition (IA-R041, Iso-Analytical Ltd.). The isotope standard alanine and our working standard acetanilide (Costech) were analyzed between aerosol samples. High precision (± 0.1 to 0.2‰) bulk $\delta^{13}\text{C}$ and $\delta^{14}\text{N}$ measurements can be made with as little as $0.5\text{ }\mu\text{mol}$ carbon and $1\text{ }\mu\text{mol}$ nitrogen (per 1–10 mg sample). Total C and N% in aerosol samples were calculated in relation to an acetanilide concentration curve performed as part of each batch of samples. To account for the possibility of atmospheric contamination, portions of glass fiber filter were run as blanks. Under the sample handling procedures outlined above, no atmospheric contamination was found.

Measurement of the $\delta^{13}\text{C}$ in CH_4 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 GC Isolink has a split post-column that sends a small ($<10\%$) split of gas to a Flame Ionization Detector (FID) and the rest to a combustion/reduction furnace with

oxidized platinum wire heated to 1030 °C, and subsequently into an open split where sample gas is diluted with He and sent to the IRMS. The $\delta^{15}\text{N}$ of the N_2 balance gas was measured by direct injection into a gas/liquid injection port on the EA coupled to the IRMS.

3. Results

3.1. Carbon isotope fractionation of methane aerosols

To better understand the preferential inclusion of one isotope over another during aerosol formation, the effect of different starting concentrations of methane was investigated. The concentrations studied and the isotopic compositions of the gas reactants and the resultant aerosol product are given in Table 2.

We report the ^{13}C of the aerosol product, defined as $^{13}\text{C} = \delta^{13}\text{C}_{\text{products}} - \delta^{13}\text{C}_{\text{reactants}}$, to describe the isotopic composition of the products relative to starting gas composition (Table 3). All four gas mixtures studied result in aerosols enriched in the heavier ^{13}C isotope, as indicated by the positive ^{13}C (Fig. 2, left axis). It is important to note that the fractionation direction toward ^{13}C enrichment is opposite that predicted by KIE theory (Nixon et al., 2012; Mandt et al., 2012), which predicts negative ^{13}C values due to faster incorporation of the lighter isotope into C_2H_2 by hydrogen abstraction from CH_4 . This is likely the result of other reactions being dominant in the production of aerosols in our laboratory study.

We note that the trend in the enrichment is similar to trends in aerosol mass yields (Trainer et al., 2006), with the observed maximum in both the fractionation and the mass yields occurring near 0.01% CH_4 . This concentration corresponds to a photochemical environment where the partial pressure of methane is high enough for sufficient reactions to occur between methane molecules, but low enough that there is sufficient photon flux to drive the formation of higher order products from secondary products. At higher CH_4 concentrations the chemistry is photon-limited, as the methane molecules absorb most or all of the UV photons, leaving few to none available for subsequent higher order reactions that lead to aerosol formation. At lower concentrations, the chemistry is methane-limited; there are plenty of photons for the higher order reactions but not enough products from methane photolysis to participate in the formation of higher order products. The apparent correspondence between yield and fractionation will be discussed in more detail in the following section.

3.2. Nitrogen isotope fractionation in aerosols

The incorporation of nitrogen in the aerosol is highly dependent on the starting methane concentration. As shown in Fig. 3 (line, right axis), as the concentration of the methane decreases, the N/C ratio increases. This can likely be attributed to the number density: at lower methane concentrations, methyl radicals will be more likely to collide with more N_2 molecules than they will be when the concentration of methane is higher. Because of this relationship, the lower CH_4 concentrations will lead to greater rates of nitrogen incorporation. These data are corroborated by prior studies: our measured N/C ratio of 0.17 ± 0.05 for a 0.1% CH_4/N_2 mixture is in direct agreement with the 0.18 determined previously (Trainer et al., 2012), and consistent with follow-on work (Yoon et al., 2014).

The second observable trend (Fig. 3, bars, left axis) is that as the N/C ratio increases, the ^{15}N value becomes more negative, signifying an increased depletion of ^{15}N atoms, and thus enhancement of ^{14}N atoms in the products relative to the N_2 gas. This result shows that the ^{14}N is preferentially incorporated into the aerosol products, possibly via an indirect N_2 dissociation mechanism such as that originally proposed in Trainer et al. (2012).

4. Discussion

4.1. ^{13}C fractionation

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. Alternative explanations for the source of the fractionation include: (1) aerosol formation pathways dependent on initial gas phase products with positive $\delta^{13}\text{C}$; (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. We discuss these possibilities below.

Determining the relationship between the gas and aerosol chemical compositions would help test the first proposed fractionation source, in which the molecules that lead to aerosol formation primarily result from a reservoir of gas-phase products that are enriched in the ^{13}C isotope (Fig. 4). In this scenario, even if the majority of products from initial CH_4 photolysis are enriched in ^{12}C due to a KIE (Fig. 4, Step 1), the aerosol molecules could be enriched in ^{13}C during secondary reactions (Fig. 4, Step 2). This is reasonable if the chemical pathways that lead to aerosol formation are dependent on molecules that are more likely to be generated with the heavier carbon isotope. The dominant gas-phase products would still exhibit a negative ^{13}C value, in part balancing the partitioning of the heavier isotope into the aerosols. Future laboratory work measuring the isotopic composition of the gas phase products (Fig. 4, dashed-line boxes) would shed some light on the possibility of fractionation in the secondary steps.

It is possible that photolysis itself was the cause of the isotope fractionation. If this were the case, the fractionation would have been caused by the rate of photolysis of ^{12}C -containing molecules versus the rate of photolysis of ^{13}C -containing molecules. This requires the chamber to have been optically thick at the photon wavelengths associated with photolysis of ^{12}C -containing molecules. While optical thickness would have limited the number of ^{12}C reactions possible, the lower abundance of ^{13}C -containing molecules would have left the chamber optically thin at photon wavelengths associated with photolysis of ^{13}C -containing molecules. This would have caused a higher rate photolysis of these ^{13}C -containing molecules. Fig. 5 (solid line) illustrates the photon flux as a function of wavelength in the chamber. N_2 photoabsorption begins at wavelengths shorter than 100 nm, so only dissociation of CH_4 occurred in this wavelength range. The CH_4 cross-section for these wavelengths is also shown in Fig. 5 (dashed line).

The difference in the zero point energy for CH_3D and $^{13}\text{CH}_4$ results in a blue shift in the methane photoabsorption cross-section of 0.9 nm and 0.04 nm, respectively (Nair et al., 2005). This blue shift will be most effective at fractionating the initial photodissociation

products in the wavelength range between 130 and 160 nm, where the cross-section is reducing with increasing wavelength (Fig. 6). The loss rate (s^{-1}) for a component due to photodissociation is simply the cross section times the photon flux. Fig. 6 illustrates the loss rate as a function of wavelength for the isotopologues of methane in this study based on the known methane cross-sections and an approximation of the expected lamp photon flux. Dissociation between 147 and 153 nm is most effective at fractionating the carbon isotopes, while dissociation between 135 and 157 nm will fractionate the D/H ratio between methane and the aerosols.

This effect may be consistent with the correlation between observed isotopic fractionation and aerosol production (Fig. 2). The fractionation of the carbon isotopes was observed in the aerosols that were produced in this study with a trend showing increased enrichment in ^{13}C with increasing aerosol production. It has been suggested that the reason aerosol formation rates decline with increasing methane concentrations beyond $\sim 0.01\%$ is due to a high optical depth in the chamber, preventing the formation of large species that can condense into aerosols. In accordance with this, as the methane concentration decreases towards 0.01% , the formation rate increases. The resulting increase in fractionation would indicate that the optical depth of the ^{13}C -species is dropping slightly faster than the ^{12}C -species, allowing ^{13}C chemical pathways to dominate the aerosol production. As methane concentrations drop below 0.01% , neither family of species is optically thick, allowing for a more equal occurrence of isotopic pathways to occur. This trend is thus supported by the demonstrated difference in isotopologue absorption cross section can be easily observed in methane (Fig. 6).

It is also possible, and probably likely, that we are observing the combined effect of the above processes. For example, at low optical depths fractionation could be dictated by aerosol nucleation rates, but fractionation at higher optical depths could be dictated by the photolysis rates of the gas-phase isotopologues. Future work in our laboratory will test these individual hypotheses.

Measurements of the small carbon-bearing molecules on Titan have not yet been made with adequate precision to distinguish the level of fractionation in the primary gas-phase products of CH_4 photolysis with respect to CH_4 (Fig. 1). Thus available data is not sufficient to differentiate between reaction steps in which fractionation may be occurring. Hopefully future observations will provide additional information on the distribution of the stable isotopes in Titan's atmosphere.

4.2. ^{15}N fractionation

As seen in Table 3, as the methane concentration decreases, the amount of nitrogen incorporated into the aerosol increases. This increase in the N/C ratio is accompanied by a decreasing, more negative ^{15}N value showing the aerosols are enriched in ^{14}N . The direction of the fractionation is the same as that observed by Kuga et al. (2014) from plasma experiments, with a slightly lower magnitude. This is not necessarily an expected result given the difference in the mechanism for nitrogen dissociation, and lower N/C ratios, in our photochemical reaction system. In the plasma, reactions are initiated by high-energy electrons. These electrons have sufficient energy to directly break the N_2 bond, without a

preferential dissociation of one isotopologue over the other. In our photolysis chamber, the low/near-zero absorption cross section of N₂ in the range of the UV-source (Chan et al., 1993), prevents the direct photolysis of N₂. Thus all the nitrogen, and associated isotopic fractionation, in our samples must be acquired through indirect reactions initialized by the photolysis of methane.

In order to evaluate the influence of chemistry involved in producing the nitrogen isotope ratio of the aerosol analogs, we return to the photon flux represented and the methane cross section in Fig. 5. Elemental analysis of the aerosol analogs produced in this process demonstrates the incorporation of nitrogen into the aerosol analogs. It is generally assumed that breaking of the molecular nitrogen bond to produce atomic nitrogen or nitrogen ions is required to incorporate nitrogen into aerosol analogs, but as stated earlier N₂ photoabsorption begins at wavelengths shorter than 100 nm, so only dissociation of CH₄ occurs in this wavelength range. At these wavelengths, methane photodissociates into five possible sets of products as listed in Table 4 (see Lavvas et al., 2011 for a review). Laboratory studies have produced a variety of results for the primary products of methane photodissociation in this wavelength range, as indicated by the branching ratios listed in Table 4. The Wang et al. (2000) scheme is commonly used in photochemical models (e.g. Krasnopolsky, 2009; Lavvas et al., 2011).

The initial products of illumination of the N₂–CH₄ mix in the chamber include H, H₂, CH, ¹CH₂, ³CH₂ and CH₃, but do not include atomic nitrogen or nitrogen ions. Therefore, atomic nitrogen must be produced at a later step. Furthermore, no ions are produced by irradiation of the N₂–CH₄ mix in this wavelength range, so neutral chemistry must be responsible for incorporating the nitrogen into the aerosol analogs. The current list of neutral reactions used in photochemical models (e.g. Lavvas et al., 2008) include two bimolecular reactions involving N₂, both of which serve to lower the energy of an excited molecule or atom:

Although (R1) could be occurring in the chamber, neither of these reactions serves to break the nitrogen molecular bond or to incorporate nitrogen into a more complex molecule. Given the pressure in the chamber, trimolecular chemistry is likely to dominate over bimolecular reactions and one trimolecular reaction currently employed in photochemical models is relevant to these conditions:

Therefore, reaction (R3) is a proposed photolysis source of nitrogen incorporation into the aerosol analogs produced in the chamber. The product yield from this reaction varies as a function of the methane abundance in the initial gas mixture. Evaluation of $\delta^{15}\text{N}$ in the aerosol analogs produced in the chamber as a function of methane abundance shows increasing enrichment in ^{14}N with increasing methane abundance, which also corresponds to increasing N/C in the aerosol products. Although other trimolecular reactions will follow (R3) that will vary depending on the methane abundance, the results suggest a fractionation in (R3) demonstrating a preference for incorporating ^{14}N into the aerosol products relative to ^{15}N .

Fractionation of the nitrogen isotopes in Titan's atmosphere has been observed to occur due to self-shielding in the atmosphere in the wavelength range between 75 and 100 nm (Liang et al., 2007), but this form of fractionation is not relevant to the results presented here as it is a result of direct N_2 photolysis.

4.3. Implications

As detailed in this study, aerosols resulting from the photolysis of methane in N_2 are enriched in ^{13}C and ^{14}N . To relate our aerosol isotopic fractionation results to those measured or calculated for gas phase reactions and other fractionation processes, we describe these results in terms of a KIE ratio, $\alpha = k_l/k_h$, where k_l is the relative rate constant for the reaction with the light isotopologue and k_h is the relative rate constant for the heavy isotopologue. These ratios are >1 if destruction of $^{12}\text{CH}_4$ or $^{14}\text{N}_2$ proceeds faster than the alternative (the so-called “normal” KIE) and <1 if the heavy isotopologue is depleted faster. Because the reactant in our flow-through system is continuously being replaced, the KIE associated with aerosol formation in this open system can be approximated by the following equation:

$$\alpha \approx \frac{R_{\text{reactants}}}{R_{\text{products}}} \tag{2}$$

where R is the ratio of heavy to light isotopes as defined in the Experimental Details section. The values for R are related to the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values reported in Table 2 using Eq. (1). With this approximation, our maximum values for α_{C} and α_{N} were found to be 0.985 and 1.006 respectively (Table 3). Comparing these derived α_{C} and α_{N} values to those used in current Titan isotopic evolution models shows some similarities and notable discrepancies (Mandt et al., 2009, 2012; Nixon et al., 2012). For example, α_{C} values used in Nixon et al. (2012) are $\alpha_{\text{C}} = 1$ for direct photolysis and $\alpha_{\text{C}} = 1.019$ for the $\text{CH}_4 + \text{C}_2\text{H}$ reaction. Mandt

et al. (2009) used $\alpha_C = 1.04$, but this was refined to $\alpha_C = 1.004$ in the later publication (Mandt et al., 2012). Our approximated α_C value is of a similar magnitude to these (absolute deviation of 1.5%), but is in the opposite direction. Our determined α_N value is in line with “normal” KIE, but is small compared to the $\alpha_N = 0.53$ that would account for the observed chemical fractionation between N_2 and HCN (Mandt et al., 2009).

When put in the context of Titan’s atmosphere, the positive ^{13}C indicates that the aerosols in Titan’s atmosphere could serve as sinks of ^{12}C . Given the observed trend in $^{12}C/^{13}C$ fractionation is opposite that predicted by the current KIE models of Titan’s atmosphere, our ^{13}C teases out an important dependence on the chemical pathways that lead to aerosol formation. This could be the result of the isotopologue-selective photodissociation shown in Fig. 6. It could also indicate that one or more of the intermediate steps prior to the condensation of the aerosols could have high isotope selectivity. It is clear that more studies are needed to elucidate which steps/intermediates in aerosol formation result in the fractionation trends observed and their relative importance compared to the other processes taking place in Titan’s atmosphere.

In the photon dominated region of Titan’s atmosphere, ~700–1600 km above the surface (Krasnopolsky, 2009), the methane concentration is ~2% (Waite et al., 2005). In this work, a maximum methane concentration of 1.5% percent in nitrogen was used. Although the optical depth is significantly different as a result of the different pressures (hundreds of kilometers for Titan versus centimeters for the chamber), photochemistry from UV is known to be a dominant source of aerosol for much of the upper atmosphere of Titan. As can be observed in our results, all of the aerosol analogs we produced have a positive ^{13}C , which suggests that photochemical aerosol formation has the potential to serve as a significant sink of ^{13}C given the high production rates on Titan. Whether the processes that control the distribution of carbon isotopes during aerosol formation are directly relevant for Titan warrants further examination. While the small gas species that have been observed (Fig. 1) appear to be unfractionated (Bézar et al., 2014), the error bars are significant and could obscure fractionation that is on the order of what we have observed in our study. Future laboratory studies investigating isotopic fractionation of the residual gas phase products will provide more insight as to mechanisms of the sequestration of C isotopes in different reservoirs as well as aerosol formation in general.

Our negative ^{15}N value is the opposite of what is observed for HCN and N_2 in Titan measurements. Our UV source does not cover the relevant wavelength range for producing the fractionation directly from N_2 , but rather shows that the previously observed incorporation of nitrogen into aerosols via lower energy pathways (Trainer et al., 2012) has a distinct isotopic preference that was previously unknown. Reaction (R3) is a proposed source of nitrogen incorporation into the aerosol analogs produced in the chamber, although there may be reactions not yet known or considered by photochemical models. This work is effectively summing over multiple termolecular neutral reactions.

On Titan, however, nitrogen chemistry and the formation of nitrogen-containing organic aerosols arises from multiple energy sources which do directly dissociate N_2 molecules: short UV and deposition of energetic electrons from Saturn’s magnetosphere. As discussed

above, in different energy regimes the behavior of isotopologues in the reaction pathways will differ. The proportion of nitrogen contributed to the aerosol mass from the indirect photolysis observed in our experiments has not yet been quantified. What can be noted here is that resultant aerosols from the indirect mechanism can trap ^{14}N and eventually settle out of the atmosphere to the surface of Titan. The remaining nitrogen would contribute to the atmosphere's enrichment in ^{15}N . If this were the case, one would expect to observe an accompanying enrichment in ^{15}N in either unreacted N_2 or more probably gas-phase products such as HCN to achieve proper mass balance. Follow up work on the isotopic composition of photolytically produced HCN relative to reactant gases and the condensed phase aerosol would shed some light on this question.

Comparing the results of our study to previous work on plasma-generated aerosols, it is important to note that while the previous study of carbon fractionation did not see a carbon isotope preference as a result of electron bombardment (Nguyen et al., 2007, 2008), our photochemically-generated aerosols that are generated in a more energy-restricted environment do show a clear carbon isotope preference. This supports the ideas presented in Fig. 6. The energies of a plasma discharge are significantly higher than those provided by photons around $\sim 150\text{nm}$ in wavelength, and could thus wipe out an observable fractionation. This would seem to indicate that dayside (photon-dominated) and nightside (plasma-dominated) chemistry follows different carbon chemical paths at an isotope level. What is surprising given the differences in carbon chemistry, is that both our photochemical aerosols and the plasma aerosols from Kuga et al. (2014) exhibit a preference for ^{14}N over ^{15}N . While our aerosols do not show the same magnitude of fractionation, the direction is the same. While our N/C ratio varied between 0.3 and 0.1, the previous study contained significantly more nitrogen (N/C between 0.9 and 0.4). Even though the two energy regimes, and probably reaction schemes, are different, larger amounts of nitrogen in the aerosol increases the amount of fractionation observed possibly reducing the amount of observed nitrogen fractionation to a numbers game, ultimately resulting in more ^{15}N gas-phase products, like HCN, left in Titan's atmosphere.

5. Conclusions

In this study, we have analyzed the carbon and nitrogen fractionation of a series of photochemically generated aerosols produced from several mixtures of CH_4 and N_2 . The resulting aerosols were enriched in ^{13}C and ^{14}N . When put in the context of Titan's atmosphere, photochemically-produced aerosols may form a sink for ^{13}C , possibly resulting from secondary reaction pathways that do not depend on the KIE. The energy dependence of this process may explain why previous studies using higher energy plasmas (Nguyen et al., 2007, 2008) did not show this trend. The enrichment of ^{14}N in the aerosols, if present on Titan, could contribute to an overall enrichment in ^{15}N in Titan's atmosphere as the condensed particles settle out. This would be consistent with the observed HCN values, through the photochemical fractionation alone is not enough to account for the magnitude of the observation. Our observed nitrogen fractionation is the similar to that observed by Kuga et al. (2014) in plasma-generated aerosols. These consistent results suggest that multiple chemical pathways of nitrogen dissociation may result in the isotopic composition of gas- and condensed-phase species. Further experiments in both areas are needed to better assess

the importance of each pathway on the global scale. In addition, these new nitrogen observations have provided a first glimpse of isotope fractionation that could be occurring during termolecular chemical reactions in the lower reaches of Titan's atmosphere.

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References

- Alexander CMOD et al., 2007 The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter. *Geochim. Cosmochim. Acta* 71, 4380–4403.
- Bézard B, Yelle R, Nixon CA, 2014 The composition of Titan's atmosphere In: Muller-Wodarg I, Griffith C, Lellouch E, Cravens T (Eds.), *Titan: Surface, Atmosphere and Magnetosphere*. Cambridge University Press, pp. 158–189.
- Chan WF et al., 1993 Absolute optical oscillator strengths for discrete and continuum photoabsorption of molecular nitrogen (11–200eV). *Chem. Phys* 170, 81–97.
- Chang S et al., 1983 *Prebiotic Organics Syntheses and the Origin of Life; Earth's Earliest Biosphere/Its Origin and Evolution*. Princeton University Press, pp. 53–92.
- Hunten DM, 1982 Thermal and nonthermal escape mechanisms for terrestrial bodies. *Planet. Space Sci* 30, 773–783.
- Krasnopolsky V.a., 2009 A photochemical model of Titan's atmosphere and ionosphere. *Icarus* 201 (1), 226–256. 10.1016/j.icarus.2008.12.038.
- Kuga M et al., 2014 Nitrogen isotopic fractionation during abiotic synthesis of organic solid particles. *Earth Planet. Sci. Lett* 393, 2–13.
- Lavvas PP, Coustenis A, Vardavas IM, 2008 Coupling photochemistry with haze formation in Titan's atmosphere, Part I: Model description. *Planet. Space Sci* 56 (1), 27–66. 10.1016/j.pss.2007.05.026.
- Lavvas PP et al., 2011 Energy deposition and primary chemical products in Titan's upper atmosphere. *Icarus* 213 (1), 233–251. 10.1016/j.icarus.2011.03.001.
- Lellouch E et al., 2014 The distribution of methane in Titan's stratosphere from Cassini/CIRS observations. *Icarus* 231, 323–337.
- Liang M-C et al., 2007 Source of nitrogen isotope anomaly in HCN in the atmosphere of Titan. *Astrophys. J* 664, L115–L118.
- Lodders K, Fegley B Jr., 1998 *The Planetary Scientist's Companion*. Oxford University Press.
- Mandt KE et al., 2009 Isotopic evolution of the major constituents of Titan's atmosphere based on Cassini data. *Planet. Space Sci* 57, 1917–1930.
- Mandt KE et al., 2012 The $^{12}\text{C}/^{13}\text{C}$ ratio on Titan from Cassini INMS measurements and implications for the evolution of methane. *Astrophys. J* 749, 160–174.
- Mandt KE et al., 2014 Protosolar ammonia as the unique source of Titan's nitrogen. *Astrophys. J* 788 (2), L24 10.1088/2041-8205/788/2/L24.
- Martins Z et al., 2007 Indigenous amino acids in primitive CR meteorites. *Meteorit. Planet. Sci* 42, 2125–2136.
- Mordaunt DH et al., 1993 Primary product channels in the photodissociation of methane at 121.6 nm. *J. Chem. Phys* 98, 2054–2065.
- Nair H et al., 2005 Isotopic fractionation of methane in the martian atmosphere. *Icarus* 175 (1), 32–35. 10.1016/j.icarus.2004.10.018.

- Nguyen M-J et al., 2007 Carbon isotopic enrichment in Titan's tholins? Implications for Titan's aerosols. *Planet. Space Sci* 55, 2010–2014.
- Nguyen M-J et al., 2008 From Titan's tholins to Titan's aerosols: Isotopic study and chemical evolution at Titan's surface. *Adv. Space Res* 42, 48–53.
- Niemann HB et al., 2005 The abundances of constituents of Titan's atmosphere from the GCMS instrument on the Huygens probe. *Nature* 438 (7069), 779–784. [PubMed: 16319830]
- Niemann HB et al., 2010 Composition of Titan's lower atmosphere and simple surface volatiles as measured by the Cassini-Huygens probe gas chromatograph mass spectrometer experiment. *J. Geophys. Res* 115 (E12). 10.1029/2010JE003659.
- Nixon CA et al., 2012 Isotopic ratios in Titan's methane: Measurements and modeling. *Astrophys. J* 749 (2), 159.
- Romani PN, 1996 Recent rate constant and product measurements of the reactions $C_2H_3 + H_2$ and $C_2H_3 + H$ —importance for photochemical modeling of hydrocarbons on Jupiter. *Icarus* 122, 233–241.
- Rousselot P et al., 2014 Toward a unique nitrogen isotopic ratio in cometary ices. *Astrophys. J* 780 (2), L17 10.1088/2041-8205/780/2/L17.
- Sebree JA et al., 2014 Titan aerosol analog absorption features produced from aromatics in the far infrared. *Icarus* 236, 146–152.
- Shinnaka Y et al., 2014 $14NH_2/15NH_2$ ratio in Comet C/2012 S1 (ISON) observed during its outburst in 2013 November. *Astrophys. J* 782 (2), L16 10.1088/2041-8205/782/2/L16.
- Smith NS, Raulin F, 1999 Modeling of methane photolysis in the reducing atmosphere of the outer solar system. *J. Geophys. Res* 104, 1873–1876.
- Trainer MG et al., 2006 Organic haze on Titan and the early Earth. *Proc. Natl. Acad. Sci* 103, 18035–18042. [PubMed: 17101962]
- Trainer MG et al., 2012 Nitrogen incorporation in CH_4 – N_2 photochemical aerosol produced by far ultraviolet irradiation. *Astrobiology* 12 (4), 315–326. [PubMed: 22519972]
- Vinatier S, Bezard B, Nixon CA, 2007 The Titan $14N/15N$ and $12C/13C$ isotopic ratios in HCN from Cassini/CIRS. *Icarus* 191, 712–721.
- Vuitton V et al., 2012 Rapid association reactions at low Pressure: Impact of the formation of hydrocarbons on Titan. *Astrophys. J* 744, 11.
- Waite JH et al., 2005 Ion Neutral Mass Spectrometer results from the first flyby of Titan. *Science* 308 (5724), 982–986. [PubMed: 15890873]
- Wang JH et al., 2000 Vacuum ultraviolet photochemistry of CH_4 and isotopomers. II. Product channel fields and absorption spectra. *J. Chem. Phys* 113, 4146–4152.
- Wilson EH, Atreya SK, 2009 Titan's carbon budget and the case of the missing ethane. *J. Phys. Chem. A* 113, 11221–11226. [PubMed: 19827852]
- Yoon YH et al., 2014 The role of benzene photolysis in Titan haze formation. *Icarus* 233, 233–241.

Fig. 1.
The $^{12}\text{C}/^{13}\text{C}$ ratios for several carbon containing compounds in Titan's atmosphere shows no significant change compared to the protosolar value (vertical dashed line), within measurement scatter and uncertainties. Adapted from data in Bézard et al. (2014).

Fig. 2.

The isotopic composition of the photochemical aerosol products are plotted as the difference in $\delta^{13}\text{C}$ in products as compared to the CH_4 reactant gas (bars, left axis). The photochemical aerosol products are enriched in the heavier ^{13}C isotope for all CH_4 concentrations studied. Previous studies with *in situ* aerosol mass spectrometry were used to quantify the dependence of aerosol mass production against CH_4 concentration (Trainer et al., 2006). These data are plotted for comparison to the isotopic signature, which may present a similar dependence on CH_4 concentration. Error bars represent a one standard deviation confidence level.

Fig. 3.

The isotopic composition of the photochemical aerosol products are plotted as the difference in $\delta^{15}\text{N}$ in products as compared to the nitrogen reactant gas (bars, left axis). At the lower CH_4 concentrations the aerosol shows enrichment in ^{14}N upon photolysis of all CH_4/N_2 mixtures. Increased enrichment of ^{14}N appears to correspond with a bulk increase in the N/C ratio of the aerosol products (line, right axis). Error bars represent a one standard deviation confidence level.

Fig. 4.

A general flow diagram for the fractionation of carbon atoms in aerosols. Even if a kinetic isotope effect leads to an enrichment of ^{12}C in gas-phase products during step (1), if the production of aerosols is dominated by molecules enriched in ^{13}C this could bias the collected aerosol product towards the heavier isotope. The remaining gas-phase products could exhibit enrichment in ^{12}C . In this diagram, the boxes drawn with solid lines represent the two reservoirs that were measured in this study. The boxes drawn with dashed-lines represent hypothetical reservoirs of carbon in our experiment for which isotopic compositions have not yet been determined.

Fig. 5.

Approximate photon flux within the chamber (solid line) is estimated from the factory-provided lamp calibration spectrum (Hamamatsu) and an estimate of the photon flux from actinometry. This is shown in comparison with the absorption cross section of methane (dashed line).

Fig. 6.
Loss rate of methane as a function of wavelength under the conditions of the laboratory study presented here.

Table 1 $^{14}\text{N}/^{15}\text{N}$ ratios of nitrogen in the Solar System.

Object	Species	$^{14}\text{N}/^{15}\text{N}$
Titan	N_2	$167\text{--}211^a$
	HCN	$58\text{--}76^a$
Protosolar	N_2	$\sim 430^{b,c}$
	NH_3	$\sim 130^{b,c}$
Terrestrial	N_2	272^d

^aBézard et al. (2014).^bShinnaka et al. (2014).^cRousselot et al. (2014).^dLodders and Fegley (1998).

Table 2

Experimental values for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ for reactant gases and aerosol products from the CH_4/N_2 mixtures used in this study, relative to internal standards.

Concentration CH_4 in N_2 (%)	$\delta^{13}\text{C}$ (‰) CH_4	$\delta^{13}\text{C}$ (‰) aerosol	$\delta^{15}\text{N}$ (‰) N_2	$\delta^{15}\text{N}$ (‰) aerosol
0.005	-43.4 ± 0.2	-35.2 ± 0.5	-1.7 ± 0.4	-8.1 ± 0.5
0.01	''	-29.1 ± 0.2	''	-4.8 ± 0.5
0.1	''	-35.1 ± 0.2	''	-2.3 ± 0.5
1.5	''	-37.8 ± 0.5	''	-0.9 ± 0.5

Table 3

Measured values for ^{13}C , ^{15}N , N/C ratios, α_{C} and α_{N} for the CH_4/N_2 mixtures used in this study.

Concentration $\text{CH}_4(\%)$	$^{13}\text{C} (\text{‰})$	$^{15}\text{N} (\text{‰})$	N/C ratio	α_{C}	α_{N}
0.005	8.2 ± 0.5	-6.4 ± 0.5	0.31 ± 0.03	0.994	0.999
0.01	14.3 ± 0.2	-3.1 ± 0.5	0.29 ± 0.05	0.991	1.001
0.1	8.3 ± 0.2	-0.6 ± 0.5	0.20 ± 0.04	0.985	1.003
1.5	5.6 ± 0.5	0.8 ± 0.5	0.13 ± 0.05	0.992	1.006

Table 4Methane photodissociation products measured in the laboratory at Lyman- α .

Products	Mordaunt et al. (1993) (scheme 1)	Mordaunt et al. (1993) (scheme 2)	Romani (1996)	Smith and Raulin (1999)	Wang et al. (2000)
$\text{CH}_3 + \text{H}$	0.51	0.49	0.41	0.41	0.29
$^3\text{CH}_2 + 2\text{H}$	0.25	0	0.21	0	0
$^1\text{CH}_2 + \text{H}_2$	0.24	0	0.28	0.53	0.58
$^1\text{CH}_2 + 2\text{H}$	0	0	0	0	0.06
$\text{CH} + \text{H}_2 + \text{H}$	0	0.51	0.10	0.06	0.07