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Titan's missing ethane: From the atmosphere to the subsurface

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ABSTRACT

The second most abundant component of the present-day Titan atmosphere, methane (CH_4), is known to undergo photolytic conversion to ethane (C_2H_6) that accumulates as a liquid on Titan's surface. Condensation temperature of ethane is higher than that of methane, so that ethane "rain" may be expected to occur before the liquefaction of methane. At present, the partial pressure of ethane in the atmosphere is 1E−5 bar, much lower than 1E−1 bar of CH_4. Estimated 8.46E17 kg or 1.37E6 km^3 of C_2H_6 have been produced on Titan since accretion. The Titan surface reservoirs of ethane are lakes and craters, of estimated volume of 50,000 km^3 and 61,000 km^3, respectively. As these are smaller than the total volume of liquid ethane produced in the course of Titan's history, the excess may be stored in the subsurface of the crust, made primarily of water ice. The minimum porosity of the crust needed to accommodate all the liquid ethane would be only 0.9% of the uppermost 2 km of the crust. The occurrence of CH_4 and liquid C_2H_6 on Titan has led to much speculation on the possibility of life on that satellite. The aggregation of organic molecules in a "primordial soup or bullion" depends in part on the viscosity of the medium, diffusivity of organic molecules in it, and rates of polymerization reactions. The temperatures on Titan, much lower than on primordial Earth, are less favorable to the "Second Coming of life" on Titan.

1. Introduction

Titan, the largest moon of Saturn, is unique in the Solar System. Whereas satellites in general are not known for having atmospheres, Titan not only possesses an atmosphere, it has a massive and complex one, harboring a suite of hydrocarbons that display a meteorological cycle similar to the hydrological cycle on Earth. The main components of Titan's atmosphere at present are nitrogen (N_2, 1.4 bar) and methane (CH_4, 0.1 bar). In Titan's atmosphere hydrocarbons are produced by the photodissociation of methane. In the stratosphere, which extends from the tropopause (approx. 40 km) to the stratopause (approx. 320 km), UV photolysis is responsible for ~1/3 of the total methane destruction (Atreya et al., 2009), 75% of which occurs at the Lyman α wavelength (121.6 nm) (Wilson and Atreya, 2009). At Lyman α, the photodissociation of methane produces other hydrocarbons, such as methyl radicals (CH_3). These hydrocarbons recombine to form heavier molecules (e.g. C_2H_6) that condense as liquids or solids in the lower stratosphere and vicinity of Titan's cold troposphere (Fig. 1) to form a haze layer and eventually precipitate from the atmosphere. In Titan's atmosphere, ethane (C_2H_6) is the main photolysis product of methane (Yung et al., 1984), with a mean production rate of 1.3×10^8 molecules cm^{-2} s^{-1} (2.16×10^{-16} moles cm^{-2} s^{-1}) from solely the photolytic conversion of methane to ethane (Wilson and Atreya, 2009), nearly tenfold the production of the other hydrocarbons combined (Toublanc et al., 1995). Higher production rates of ethane (Cornet et al., 2015), $1.2–15 \times 10^9$ molecules cm^{-2} s^{-1}, are either similar or higher than the photochemical removal rate of CH_4, 2.5×10^9 molecules cm^{-2} s^{-1} (Wilson and Atreya, 2009). A simplified sequence of direct forward reactions from CH_4 to C_2H_6 that short-circuit the complex intermediate paths can be represented by the following (Gilliam et al., 2015):

$CH_4 \rightarrow CH_3 + H$ first-order rate parameter k_{12} (s^{-1}),

$$d[CH_4]/dt = F - k_{12}[CH_4] \tag{1}$$

$$d[CH_3]/dt = k_{12}[CH_4] \tag{2}$$

$CH_3 + CH_3 \rightarrow C_2H_6$ 2nd-order rate parameter

$$k_{23}\ (\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}),\ d[C_2H_6]/dt = k_{23}[CH_3]^2 \tag{3}$$

$C_2H_6 \rightarrow$ other products first-order rate parameter k_3 (s^{-1}),

$$d[C_2H_6]/dt = -k_3[C_2H_6] \tag{4}$$

where [ ] are atmospheric concentrations in kg, mol or molecules vol^{-1}, k_{ij} are the reaction rate parameters, and $F \geqslant 0$ (mass vol^{-1}

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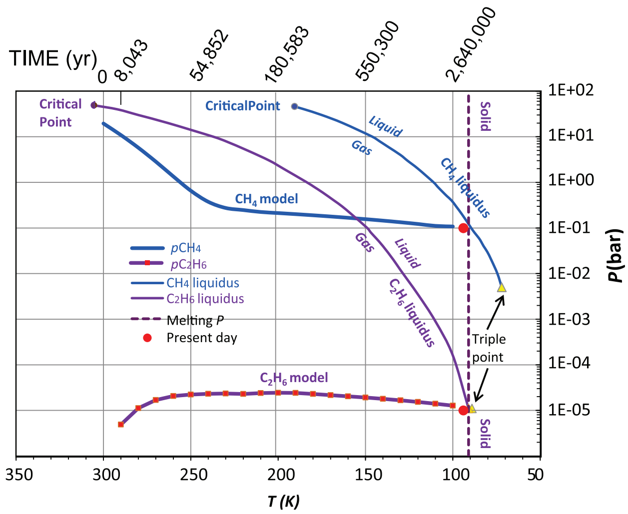

Fig. 1. One of the important points in the history of methane and ethane in Titan's atmosphere is that C_2H_6 condenses at a higher temperature than CH_4. The figure above shows: (a) saturation vapor pressure or liquidus curves of each gas (CRC Handbook of Chemistry and Physics, 2016). Note that as Titan's atmosphere cools from about 300 K down, C_2H_6 liquefies before CH_4 and it also forms a solid phase at the triple point before CH_4. Thus liquefaction and "raining" of C_2H_6 in Titan's atmosphere is expected to begin before that of CH_4. (b) Calculated partial pressures of methane and ethane in the theoretical reactions sequence (1)–(4), as explained in the text. Present-day partial pressures are shown as red dots. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

time^{-1}) is the rate of CH_4 emission from the interior to the atmosphere. The resulting ethane is largely shielded from UV radiation by methane and acetylene (C_2H_2), making it stable against photolysis. The principal loss mechanism for ethane is condensation at the tropopause, followed by its accumulation as a liquid on the surface (Yung and DeMore, 1999).

Another mechanism of methane loss in the Titan atmosphere is hydrodynamic escape. First observed by the Voyager spacecraft and confirmed by the Cassini Ion Neutral Mass Spectrometer (INMS), the methane distribution in Titan's upper atmosphere remains uniformly mixed to the altitude of ~1100 km, where it begins to exhibit diffusive separation. Further evidence from the Cassini INMS suggested that methane is not well mixed to high altitudes (>1000 km) because of a large escape rate, 2.9×10^9 molecules cm^{-2} s^{-1} (4.8×10^{-15} moles cm^{-2} s^{-1}) (Yelle et al., 2008). The most likely mechanism is hydrodynamic escape – a high density, slow outward expansion driven mainly by solar UV heating due to CH_4 absorption (Strobel, 2009) – as evident from heating rates gathered from the Huygens Atmospheric Structure Instrument (HASI). This loss rate is responsible for 22% of the total methane loss rate (Wilson and Atreya, 2009).

The third mechanism of methane loss is thermal escape, where the outgoing methane flux is proportional to the methane mass in the atmosphere and it depends on temperature, gas molecular mass, atmosphere thickness, and Titan's escape velocity (Gilliam and Lerman, 2014a; Gilliam et al., 2015).

Consideration of these processes suggests that Titan should have produced a substantial amount of ethane since accretion. Such an idea was first proposed by Lunine et al. (1983), who used photochemical models to predict that Titan would be covered by an ethane ocean one to several kilometers deep, and was later supported by others' models, albeit with a smaller net volume of ethane produced. Further, Mousis and Schmitt (2008) proposed a geological process that resolves "the ethane deficiency issue in a manner which is in agreement with our current knowledge of Titan: the incorporation of liquid hydrocarbons in the porous cryovolcanic subsurface". However, Cassini–Huygens observations have not shown evidence of widespread surface ethane reservoirs.

This paper addresses three issues: (1) the mass and volume of ethane that was produced on Titan since accretion, based on the production-rate estimates of other investigators; (2) the occurrence of liquid ethane in the surface depressions (craters and lakes) and in the crustal subsurface; and (3) the physical characteristics of liquid ethane as a potential medium for emerging life. To address the first issue, we present a straightforward photochemical model using primordial conditions presented in Gilliam and Lerman (2014a,b) and compare our results to the latest observations from the Cassini mission.

2. CH_4 depletion and C_2H_6 production through time

The condensation temperature of ethane is lower than that of methane, as shown by the two liquidus curves in Fig. 1. Thus liquefaction and "raining" of C_2H_6 in Titan's atmosphere is expected to begin before that of CH_4 (Sagan and Thompson, 1984; Barth and Toon, 2003; Rannou et al., 2006; Lunine and Atreya, 2008). The cooling time of Titan's surface, calculated assuming heat dissipation by radiation emission from an ideal black body, from the initial accretion temperature of 300 K to 100 K is about 3×10^6 years (Gilliam and Lerman, 2014a).

Atmospheric observations and numerous other works have shown that ethane does condense at higher altitudes than methane. However, there are two other possible compositions of the rain on Titan. Graves et al. (2008) considered condensation of N_2–CH_4–C_2H_6, based on N_2 being the main component of Titan's atmosphere at present. Mousis and Schmitt (2008) have also discussed the possibility of CH_4–C_2H_6–N_2 liquid condensing on the Titan surface. Atreya et al. (2006) concluded that C_2H_6 condenses at altitudes above the tropopause where the temperature is near 70 K. Croft et al. (1988) have reported that water–ammonia solutions remain liquid down to 190–170 K, which suggests that if NH_3 was a component of the atmosphere in the past, an H_2O–NH_3 rain main have carried dissolved CH_4 and C_2H_6 to the surface.

With regard to liquid N_2 in Titan's atmosphere, its condensation temperature at the pressure of 1–2 bar is 77–82 K, below the 90 K of the present-day Titan surface (CRC, 2016). However, N_2 dissolves in methane–ethane mixtures (Farnsworth et al., 2016) and it forms hydrous clathrates in the temperature range from 215 K to 375 K (van Hinsberg and Schouten, 1994). If precipitation of a liquid mixture of C_2H_6–CH_4–N_2 was taking place on Titan, the total mass condensed over the lifetime of the satellite would have been greater than that of C_2H_6 alone. However, the solubility of N_2 in C_2H_6 is very low (Chevrier et al., 2015; Farnsworth et al., 2016), and it is the presence of CH_4 in the CH_4–C_2H_6 liquid mixture that promotes dissolution of N_2.

The two model curves for the evolution of CH_4 and C_2H_6 in Fig. 1 are a theoretical example of a model of the four simultaneous reactions (1)–(4). The model includes input of CH_4 from the interior to the atmosphere, at the rate of $F = 4.13 \times 10^{13}$ kg/yr or 5.46×10^{14} molecules cm^{-3} yr^{-1}. This rate of input was used to calculate the history of thermal escape of CH_4 from Titan's atmosphere in a model of input with escape (Gilliam and Lerman, 2014a). Among other estimates of the CH_4 emission rate from the interior, the input cited operated for 57,350 yr; if it continued indefinitely, it would have exhausted the CH_4 reservoir in Titan's interior in about 6×10^6 yr. This is longer than the 3×10^6 yr for the surface temperature to cool to 100 K. The model results were also based on emission rates lower by a factor of 100, with a correspondingly longer time to exhaustion of the CH_4 reservoir.

The rate constants of reactions (1)–(4) are from the ranges given by Yung and DeMore (1999, p. 219), Wilson and Atreya (2004, Fig. 13) and Atreya et al. (2009); and compilation in