

Organic chemistry on the surface of Titan

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Abstract Some aspects of Titan's organic chemistry are considered with particular emphasis on possible surface processing of organic species made in Titan's upper atmosphere. Sources of energy include solar ultraviolet radiation, charged particles from the Saturnian magnetosphere, cosmic rays, winds and rain, hypervelocity impacts and (putatively) melting of crustal water ice (cryovolcanism). All of these sources, even those for which the energy is absorbed in the upper atmosphere, affect the surface, either directly or through the deposition of chemically reactive species sedimented out of the atmosphere in the form of aerosols. Once on the surface, organic molecules are immersed in a variety of different environments including dunes, mountains, river valleys, lakes and seas, which will affect the nature and outcome of chemical processes. All of the liquids in these environments are the light alkanes: methane, ethane, and propane. The organic chemistry ongoing in the surface system, should it be accessible for study, would provide an object lesson in the extent to which planetary environments drive or inhibit chemical complexity, with obvious application to the prebiotic Earth.

Keywords Organic molecules · Solar system · Titan · Saturn system · Cosmic rays · Organic chemistry

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1 Introduction

Titan is the most organic-rich extraterrestrial body in the solar system, with an inventory expressed in terms of mass per area that rivals the non-carbonate organic reservoirs on the Earth (Lorenz et al. 2008). Much of the known carbon is gaseous, in the form of methane, forming the second most abundant molecule after molecular nitrogen in the atmosphere. There is a rich literature on Titan, thanks to the Cassini-Huygens mission, and any reasonably complete compendium requires a book-length treatment (Brown et al. 2009). What is important here is the instability of methane against chemical conversion to higher order hydrocarbons and (with nitrogen) nitriles, timescales that are short compared to the age of the solar system and, presumably, Titan. The conversion is made possible by a variety of energy sources, some of which are operative on the surface and some in the atmosphere. But even the atmospheric conversion leaves its legacy on chemistry of Titan's surface in the form of potentially unstable compounds that, once an activation energy barrier is overcome, can undergo further conversion. The products of the methane chemistry also alter the composition of the lakes and seas of liquid hydrocarbons found at high latitudes and provide the raw material for the vast equatorial belt of dunes composed of solid organics.

In this short paper we examine the potential for interaction between Titan's geology and the products of organic chemistry ongoing in the atmosphere and on the surface, drawing on a number of recent Cassini observation and experimental studies by various groups. Despite the very low surface temperature of 94 K at the equator (essentially fixed) and approximately 90 K near the poles (variable by only a few degrees seasonally), the potential for interesting organic chemistry modified, even energized, by surface processes makes Titan a high-priority target for continued exploration after the Cassini-Huygens mission.

2 Sources of energy

Figure 1 shows schematically the sources of energy available for chemistry in Titan's atmosphere and the approximate altitudes at which each form of energy (ultraviolet, charged particle) is absorbed. Also depicted is the temperature profile with altitude, which is crucial to the behavior of chemical products in Titan's atmosphere. The steep positive temperature gradient in the stratosphere, a result of the absorption of blue photons from the Sun by atmospheric aerosols, ensures that a wide variety of intermediate products of methane chemistry condense somewhere in the stratosphere, isolating them from further atmospheric processing. These aerosols continue to grow, and descend, eventually becoming nucleating seeds for ethane (lower stratosphere) and methane (troposphere) ices. At low altitudes the ethane, methane and propane melt, perhaps soaking into the surface or flowing into cracks, while the solid residues in the aerosols coat the surface. The subsequent histories of the two different phases are poorly known but we have some clues that they are complex; we return to this question in Sect. 3.

Titan's dense lower atmosphere (the surface air density is 4.5 times that of air at sea level on the Earth), and large column abundance of gas screen out almost all sources of energy (ultraviolet, charged particle) that would further process the organic deposits into very refractory, hydrogen-poor material. In this sense Titan is very different from that of most other solid bodies in the solar system that have surface organics—typically these organics are “cooked” to produce what is often referred to in the terrestrial case as

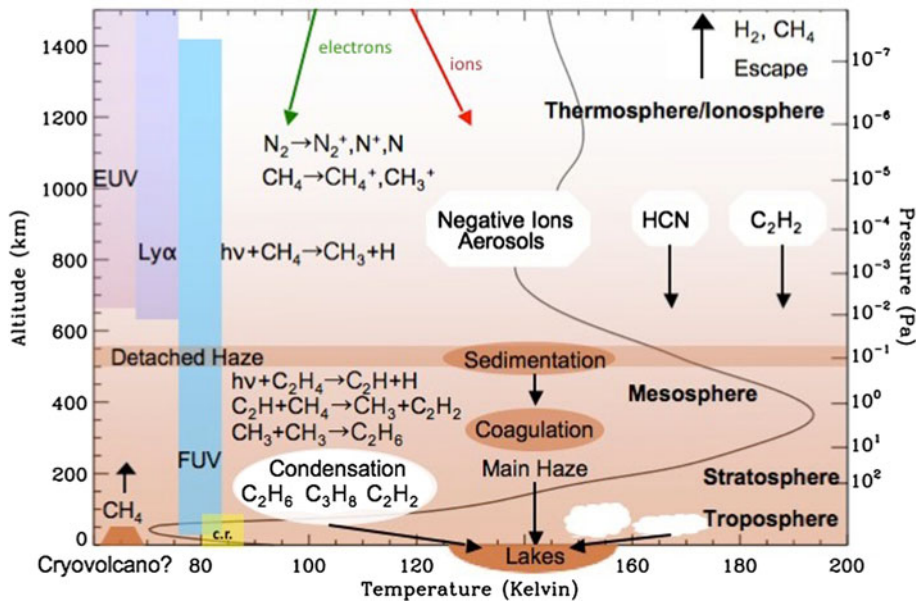


Fig. 1 The deposition of energy in Titan's atmosphere from various sources within and outside the Saturn system. The temperature versus altitude in kilometers and pressure in Pascals is shown, along with the detached haze layer. The main atmospheric layers are shown. Aerosol particles in the haze sediment and coagulate, ending up on the surface in the dunes, lakes and seas. Solar ultraviolet radiation is deposited at various level in the atmosphere according to wavelength; here it is divided schematically into extreme-ultraviolet (up to 1200 Å), Lyman- α (1215.668 Å) and far-ultraviolet (from 1200 Å to the visible). The altitude range of deposition of cosmic rays ("c.r.") is also shown. In the upper atmosphere electrons and ions from the Saturnian magnetosphere and the solar wind drive ion chemistry and generate an ionosphere; evidence for negative ions and very high altitude aerosols are seen above 900 km. Methane is photolyzed at and above the mesosphere producing acetylene and hydrogen cyanide as primary products. Methane is lost by photolysis, and also by direct escape to space in the thermosphere. It may be resupplied from subsurface crustal sources and deeper water ice (cryo) volcanism, and forms clouds in the troposphere; ethane may form aerosol clouds in the lower stratosphere. Other reactions producing higher hydrocarbons and nitriles occur deeper in the atmosphere where acetylene and other species are broken apart by FUV radiation. Figure is based on original figures by Roger Yelle (pers. comm.) and Bernard (2004)

kerogen. Other exceptions include the Earth, where photosynthesis generates new organic compounds from carbon dioxide and water, even while a large residue of kerogen competes with carbonates as the dominant organic crustal reservoir (Lorenz et al. 2008), and some Kuiper Belt objects (in which we include Triton and Pluto), on which seasonal cycling tends to remove methane from the sunlit surface and deposit it on the winter (unlit) regions.

There are five sources of energy available for surface chemistry: (a) cosmic rays, (b) acetylene cyclization to benzene, (c) impacts, (d) cryovolcanism and (e) meteorology. The cosmic ray energy flux at Titan's surface is of order 10^{-3} ergs cm^{-2} s^{-1} . The ultraviolet energy flux available for methane photolysis in the upper atmosphere of Titan is of order 0.1 ergs cm^{-2} s^{-1} derived from (Yung et al. 1984). The cosmic ray energy flux at the surface is coincidentally not dissimilar to the energy flux due to magnetospheric particles at the top of the atmosphere, but is energizing condensed surface chemistry rather than gas phase processes. Also, the cosmic rays reaching the surface are the highest energy (>30 GeV) particles; hence the *particle* flux (number / area / time) is low. The conversion of

acetylene to benzene releases as much as 190 kJ of energy per mole of acetylene (Zhou et al. 2010). This is the primary pathway by which solar ultraviolet energy is brought to the surface; that is, by the transformation of alkanes into alkynes followed by sedimentation to the surface. The conversion of methane to acetylene requires about 334 kJ mol^{-1} acetylene (McKay and Smith 2005). Since about 6% of the methane has been converted to acetylene in the stratosphere, this implies that 3% of the solar UV absorbed in the stratosphere is being carried to the surface in the form of the unsaturated bond in acetylene, equivalent to an energy flux of order $10^{-3} \text{ erg cm}^{-2} \text{ s}^{-1}$, comparable to the energy flux due to cosmic rays.

Impact of asteroidal or cometary bodies is a pervasive process in the solar system and the impact rate through time is approximately known for the Saturn system through the cratering record on airless Saturnian moons (Wood et al. 2010). The impactor flux would have been highest in the first few hundred million years of Titan's history, declining steeply before a significant amount of surface deposition of products of methane photochemistry occurred. However, it has been proposed that Titan's current atmospheric inventory of methane has been supplied by an impactor or impactors with total kinetic energy of between 10^{23} – 10^{24} kJ. To maintain the methane supply over the age of the solar system, about 10 or 20 such events are needed, for an upper bound to the kinetic energy of order 10^{25} kJ. The release of energy per unit area per unit time averaged over the age of the solar system is then of order $1 \text{ erg cm}^{-2} \text{ s}^{-1}$, a thousand times that of the other sources, but highly heterogeneous in location and time. Further, some of the energy is radiated immediately in the impact process so that the amount trapped as heat in the surface, available for chemistry, may be a tenth of this value (Lunine et al. 2009).

Because Titan is a mixed rock and water ice body, with most of the ice concentrated in outer layers, there is the possibility that the ice may be melted by internal heat sources, probably in the presence of impurities that act as antifreezes, in a process referred to as cryovolcanism (Mitri et al. 2008). The energy available from this process is unknown for Titan: it could be zero (no cryovolcanism; heat transported by conduction) or a significant fraction of Titan's estimated crustal average heat flow of $5 \text{ erg cm}^{-2} \text{ s}^{-1}$ (Nimmo and Bills, 2010). In contrast the available energy from sunlight for near-surface atmospheric convection is estimated to be 200 times larger than the crustal heat flow. However, surface deposits see this energy only indirectly, in the form of particle movement associated with winds and running liquid methane along channels after rainstorms.

3 Surface chemistry associated with sources of energy

Photosynthesis on Earth captures only roughly $200 \text{ erg cm}^{-2} \text{ s}^{-1}$ of the roughly $10^6 \text{ erg cm}^{-2} \text{ s}^{-1}$ available as sunlight at the top of the Earth's atmosphere (FAO 2005). Therefore, we should not expect Titan surface organics to utilize more than a fraction of the energy available from the sources listed above. The nature of the possible reactions will be very different for the different sources as well. Some or all of the energy available from cosmic rays may go into raising the acetylene to the triplet excited state, from which benzene formation can occur without the impediment of a substantial activation energy barrier (140 kJ mol^{-1}) present to the ground state conversion of acetylene to benzene (Zhou et al. 2010). In addition, hydrogen cyanide is produced in Titan's atmosphere in comparable abundance to acetylene (Lavvas et al. 2008); reaction of HCN with C_2H_2 yielding C_3HN or CH_3CN might be energized by cosmic rays and/or acetylene polymerization. Both C_3HN and CH_3CN appear to be present in near-infrared spectra of Titan's surface along with benzene, while hydrogen cyanide and acetylene are mostly absent

(Clark et al. 2010). The last of these does however appear to be present in the surface around the Huygens landing site (Niemann et al. 2010). Thus, the Cassini-Huygens mission may already be giving us evidence that chemistry at Titan's surface is modifying the abundances of hydrocarbons produced in the atmosphere.

Titan's methane–ethane lakes and seas cover roughly 1% of the surface, concentrated at high northern latitudes. Because of a reasonably high solubility of a number of species in the hydrocarbon liquid (Cordier et al. 2009; Raulin et al. 2010), chemistry energized by cosmic rays may produce other compounds from the dissolved compounds, that may then precipitate to the sediments at the bottom of the lakes. Methane may cycle seasonally from one hemisphere to the other, reducing the extent of the shallower lakes and exposing sediments on the periphery; orbital variations (Aharonson et al. 2009) will do the same on longer timescales leaving large numbers of lake sediment basins exposed on the dry hemisphere (Fig. 2).

Fluvial erosion by liquid methane has produced channels on size scales from meters to hundreds of meters on Titan's surface, fed by methane rainfall which may have been observed by Cassini in both polar and equatorial regions of Titan (Turtle et al. 2011). Pebbles ranging in size from 3 mm (the resolution limit of DISR) to 15 cm observed at the Huygens landing site (Tomasko et al. 2005) were likely deposited by liquid methane draining from the hills a few kilometers from the site, where the channels were seen (Fig. 3). Based on estimated precipitation rates (Hueso and Sanchez-Lavega 2006) and the observed channel properties (Tomasko et al. 2005) the average flow velocity would be approximately 10 m/s. The mechanical action of methane flowing in the channels during storms could act to scour acetylene and other solid deposits from the streambed. Since agitation of solid acetylene in the lab is known to cause it to explosively polymerize (Matteson 1983), agitation associated with running methane and the pebbles transported by it could encourage chemistry in situ, either forming benzene from the acetylene or causing

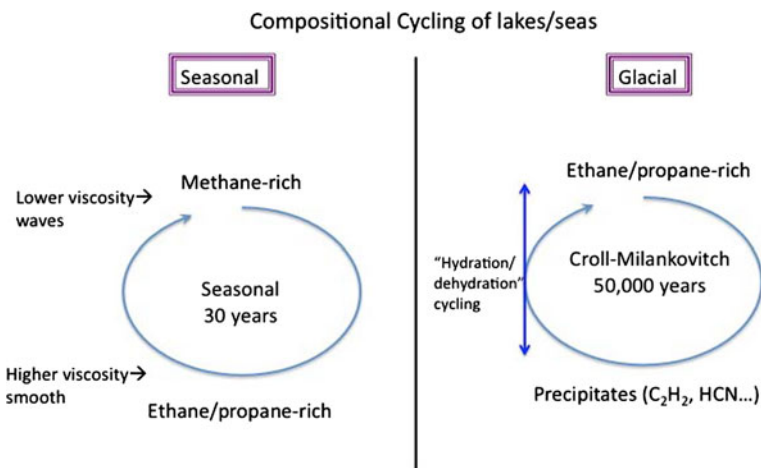


Fig. 2 Cycling of Titan's lakes on seasonal (*left*) and orbital "glacial" timescales (*right*) Titan's year is 30 Earth years and the orbital cycles are of order 100,000 Earth years. On seasonal timescales lakes go from methane-rich to methane-poor, changing the viscosity of the lakes (Lorenz et al. 2010) and exposing the peripheries of shallower lakes. Variations in the phasing of seasons and Titan's perihelion date may lead to complete evaporation of ethane from smaller lakes (Aharonson et al. 2009) and exposure of the lake bottom deposits containing products of cosmic ray energized lake chemistry

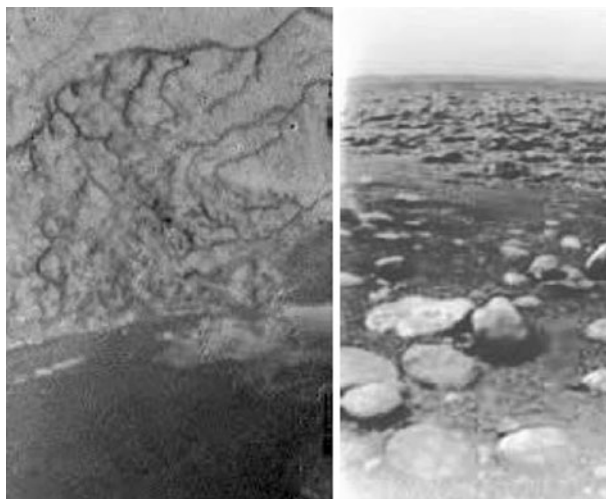


Fig. 3 *Left* Fluvial features over ~ 20 square km area seen at 30 meters resolution from the Huygens Descent imager and spectral radiometer. *Right* Pebbles typically a few cm in size dot the Huygens landing site. Both images courtesy ESA/NASA/JPL/U. Arizona

reactions with other organic compounds in solution. These would then be deposited in the outwash, including at the Huygens site.

In the region around a large impact site, interaction between the organics and extensive amounts of melted water ice will occur (Lunine et al. 2010), possibly leading to the formation of oxygen-bearing organic molecules, including amino acids (Neish et al. 2010); addition of ammonia expands the product range (Ramirez et al. 2010). The surface is not the only site where amino acids may form on Titan; simulations suggest that gas phase chemistry may produce them as well (Hörst et al. 2010).

Future spectroscopic observations with higher spatial and spectral resolution than available from Cassini may reveal the presence of chemically altered lake-bottom sediments, channels in which methane flows violently after storms, and oxygenated organic compounds in and around impact sites. Balloon-borne or landed probes may be required to diagnose in detail the organic phases and their geological contexts (Stofan et al. 2010; Lunine et al. 2011). The organic chemistry ongoing in the surface system, should it be accessible for study, would provide an object lesson in the extent to which planetary environments drive or inhibit chemical complexity, with obvious application to the pre-biotic Earth in spite of many differences.

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