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Note

Possibilities for methanogenic life in liquid methane on the surface of Titan

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Abstract

Photochemically produced compounds on Titan, principally acetylene, ethane and organic solids, would release energy when consumed with atmospheric hydrogen, at levels of 334, 57, and 54 kJ mol^{-1}, respectively. On Earth methanogenic bacteria can survive on this energy level. Here we speculate on the possibility of widespread methanogenic life in liquid methane on Titan. Hydrogen may be the best molecule to show the affects of such life because it does not condense at the tropopause and has no sources or sinks in the troposphere. If life is consuming atmospheric hydrogen it will have a measurable effect on the hydrogen mixing ratio in the troposphere if the biological consumption is greater than 10^8 cm^{-2} s^{-1}. Life could develop strategies to overcome the low solubility of organics in liquid methane and use catalysts to accelerate biochemical reactions despite the low temperature. The results of the recent Huygens probe could indicate the presence of such life by anomalous depletions of acetylene and ethane as well as hydrogen at the surface.

Keywords: Titan; Life; Methanogens

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1. Introduction

Titan has an atmosphere with 50% more surface pressure than the Earth, composed of nitrogen with a few percent methane and a tenth of a percent of hydrogen (e.g., Lellouch et al., 1989). Photochemical processes in the upper atmosphere generate a rich gas phase organic chemistry of hydrocarbons and nitriles as observed by Voyager (Hanel et al., 1981; Maguire et al., 1981; Kunde et al., 1981). In addition Titan's atmosphere holds an optically thick organic haze (e.g., McKay et al., 2001). These photochemical products on Titan represent a disequilibrium state and a potential source of chemical energy. On Earth life uses only two types of energy for primary production: sunlight and chemical energy. Thus, the presence of chemical energy in the form of organics in the atmosphere of Titan is of interest with respect to speculations about life on that world.

Previous speculations regarding life on Titan have focused on the possibility of water-based life similar to life on Earth (Thompson, W.R., Sagan, C., Stevenson, D., Wing, M., 1992. Impact mediated chemical evolution on Titan. Bull. Am. Astron. Soc. 24. Poster; Fortes, 2000; Simakov, 2004). However water is not commonly present as a liquid on the surface of Titan since the average temperature is 95 K and thus these authors have postulated subsurface life. Hence, if water-based life is, or was, present on Titan its effects would be hard to detect. The water-based life on Earth has global effects because water is globally distributed on this planet. Similarly, if there was life based on liquid methane on Titan it could be widespread on the surface and have global effects.

Experiments investigating the solubility in liquid ethane of organic material (tholin) produced in laboratory simulations of Titan's atmosphere have indicated very low solubility. McKay (1996) found that tholin was insoluble in liquid ethane at the level of measurement (0.03% by mass). Tests in a variety of solvents (McKay, 1996) revealed that tholin material is much more soluble in polar solvents (water, ethanol, methanol, glycol, and dimethylsulfoxide) than in non-polar solvents (ethane, hexane, benzene). This result is consistent with the theoretical work by Raulin (1987). Coll et al. (1999) confirmed these results and also found that the tholin material was soluble in acetonitrile at levels of 0.4%, and in other nitriles as well. Although liquid methane has not been directly tested the results listed above would lead to the conclusion that tholin has low solubility in liquid methane. This has discouraged speculation regarding life in liquid methane on Titan. Schulze-Makuch and Irwin (2004) have discussed the possibility of life in organic solvents.

2. Results

While acknowledging the potential problem of solubility in liquid methane we have computed the energetics of possible methane-based life on Titan. Sunlight on Titan produces complex hydrocarbons (C_2H_2, C_2H_6,

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Table 1
Free energies of hydrogenation on Titan

Reaction	$-\Delta G$ (kJ mol^{-1})
$C_2H_2 + 3H_2 = 2CH_4$	334
$C_2H_6 + H_2 = 2CH_4$	57
$R–CH_2 + H_2 = R + CH_4$	54

Table 2
Heats of formation and entropy at standard conditions (25 °C, 1 bar)

Molecule	H (kJ mol^{-1})	S (J/mol K)
CH_4(g)	−74.8	186.3
H_2(g)	0	130.58
C_2H_2(g)	226.7	200.8
C_2H_6(g)	−84.68	229.5
C_3H_8(g)	−103.85	269.9
$R–CH_2$	−19.17	40.40

and organic haze) that could be a source of energy when reacted with atmospheric hydrogen. This is in direct analogy with the potential chemical energy in organics on Earth when reacted with atmospheric oxygen.

In Table 1 we show the Gibbs free energy, ΔG, released from three reactions computed for Titan conditions using the method described by Kral et al. (1998). The energy released from a reaction is given by

$$\Delta G = \Delta H - T\Delta S + RT\ln(Q),$$

where ΔH and ΔS are the difference in heats of formation and entropy at standard conditions between the products and the reactants, R is the universal gas constant, T is the temperature, and Q is the ratio of the activities of each product to each reactant raised to the power of their multiplying constant in the reaction equation. For example for the C_2H_2 reaction,

$$Q = [pCH_4]^2/[pC_2H_2][pH_2]^3.$$

The chemical activities of gases are approximately equal to their partial pressure. The activity of solid tholin is unity. We use a surface pressure of 1.5 atm, temperature of 95 K, and partial pressure of CH_4, H_2, C_2H_6, and C_2H_2 of 5%, 0.1%, 10 ppm, and 1 ppm, respectively. The last reaction represents the simplest reaction for the hydrogenation of the solid organic haze material by the removal of one surface CH_2 group and the production of CH_4. Table 2 lists the standard heats of formation and entropy for several compounds of interest (CRC, 1976). The free energy and entropy of C_2H_8 is listed for comparison with C_3H_6. The difference between these two shows an example of the free energy and entropy change due to the removal of one CH_2 group. It is known that for a range of organic molecules (normal alkyl cyclohexanes, normal alkyl benzenes, normal alkyl cyclopentanes, normal monoolefins and normal acetylenes) the energy of formation and the entropy difference for the removal of a CH_2 group is roughly constant and we use these typical values for the tholin hydrogenation reaction in Table 2.

3. Discussion and conclusions

The free energies released by the reactions in Table 1 compare favorably to the minimum energy required to power methanogen growth on Earth of ~10 kcal mol^{-1} (42 kJ mol^{-1}) determined by Kral et al. (1998). Energetically, life on the surface of present Titan is plausible with C_2H_2 providing the best energy source. If life on Titan were to consume H_2 until the free energy available were comparable to the limit of H_2 uptake by methanogens on Earth, 42 kJ mol^{-1}, then the concentration of H_2 would drop by a factor of more than 1000 at the surface due just to biological consumption.

If bacteria are consuming complex hydrocarbons at the surface of Titan, the observable effects might include: complete consumption of C_2H_2 at the surface, reduction in C_2H_6 and organic solids at the surface compared to the accumulation expected from photolysis alone, and a sink of hydrogen at the surface creating a gradient in the hydrogen mixing ratio with altitude. All of these effects may be detected and measured by the Huygens probe. Using a photochemical model of Titan's atmosphere (Lebonnois et al., 2003) it is possible to compute the H_2 mixing ratio at the surface of Titan as a function of the strength of a biological sink at the surface. Other photochemical models (e.g., Wilson and Atreya, 2004) which have similar source terms for H_2 give similar results even if other details of the photochemistry are different. The biological signature should be most clear for H_2 because it has no photochemical sources or sinks in the troposphere and does not condense at the tropopause. Fig. 1 shows the computed mixing ratio of hydrogen at the surface for a range of values of the biological flux. For biological fluxes below 10^8 cm^{-2} s^{-1} the effect is small while for biological fluxes greater than 10^9 cm^{-2} s^{-1} the hydrogen mixing ratio becomes vanishingly small. Clearly, measurements of the H_2 mixing ratio by the mass spectrometer on the Hyugens probe could detect reductions in the concentration of H_2 that correspond to a strong biological sink.

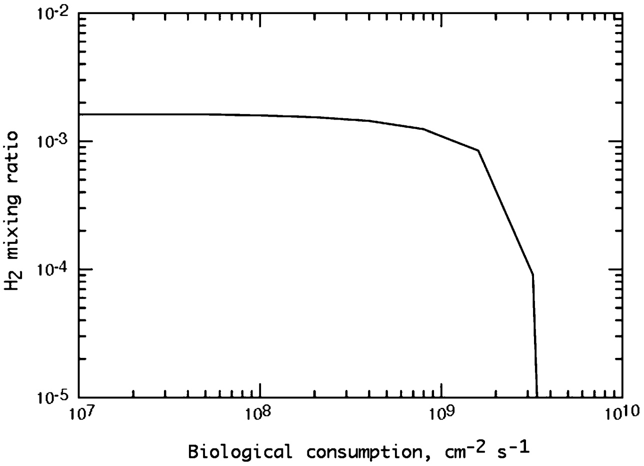

Fig. 1. Computed mixing ratio of hydrogen at the surface of Titan as a function of the biological consumption at the surface using a standard photochemical model (Lebonnois et al., 2003).

If microorganisms on Titan were catalyzing the production of CH_4 from C_2H_2 and C_2H_6 then this could represent a significant source of CH_4 partially explaining the presence of CH_4 in the troposphere of Titan despite the apparent absence of a surface ocean or lakes as imaged during the recent Cassini encounters (e.g., Porco et al., 2005). It is interesting that methane on Titan, is found to be isotopically lighter than would be expected from theories of Titan's formation (Lunine et al., 1999), which could be a sign of microbial fractionation (Abbas and Schulze-Makuch, 2002).

Although we have shown here that the energetics of methane-based life on Titan may be favorable there are two important difficulties to consider related to such life forms. First, the low temperatures imply very low rates of reaction. However by the use of catalysts life can speed up any thermodynamically favorable reaction. The second, more problematic issue is the low solubility of organic substances in liquid methane. Because water is such an excellent solvent we have no experience with how life adapts and works with sparse solubility. It is possible that active transport and organisms with large surface to volume ratios could mitigate this problem.

Titan is a world with a surface that contains a widespread liquid and abundant chemical energy produced by sunlight. If life has evolved in this environment its effects, as on Earth, are unlikely to be subtle.

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References

Abbas, O., Schulze-Makuch, D., 2002. Acetylene-based pathways for prebiotic evolution on Titan. ESA Spec. Publ. SP-518, 345–348.

Coll, P., Coscia, D., Smith, N., Gazeau, M.-C., Ramirez, S.I., Cernogora, G., Israël, G., Raulin, F., 1999. Experimental laboratory simulation of Titan's atmosphere: Aerosols and gas phase. Planet. Space Sci. 47, 1331–1340.

CRC, 1976. Handbook of Chemistry and Physics, 57th ed. CRC Press, Boca Raton, FL.

Fortes, A.D., 2000. Exobiological implications of a possible ammonia—Water ocean inside Titan. Icarus 146, 444–452.

Hanel, R., 15 colleagues, 1981. Infrared observations of the saturnian system from Voyager 1. Science 212, 192–200.

Kral, T.R., Brink, K.M., Miller, S.L., McKay, C.P., 1998. Hydrogen consumption by methanogens on the early Earth. Origins Life Evol. B. 28, 311–319.

Kunde, V.G., Aikin, A.C., Hanel, R.A., Jennings, D.E., Maguire, W.C., Samuelson, R.E., 1981. C_4H_2, HC_3N, and C_2N_2 in Titan's atmosphere. Nature 292, 686–688.

Lebonnois, S., Bakes, E.L.O., McKay, C.P., 2003. Atomic and molecular hydrogen budget in Titan's atmosphere. Icarus 161, 474–485.

Lellouch, E., Coustenis, A., Gautier, D., Raulin, F., Dubouloz, N., Frère, C., 1989. Titan's atmosphere and hypothesized ocean: A reanalysis of the Voyager 1 radio-occultation and IRIS 7:7 μm data. Icarus 79, 328–349.

Lunine, J.I., Yung, Y.L., Lorenz, R.D., 1999. On the volatile inventory of Titan from isotopic abundances in nitrogen and methane. Planet. Space Sci. 47, 1291–1303.

McKay, C.P., 1996. Elemental composition, solubility, and optical properties of Titan's organic haze. Planet. Space Sci. 44, 741–747.

Maguire, W.C., Hanel, R.A., Jennings, D.E., Kunde, V.G., Samuelson, R.E., 1981. C_3H_8 and C_3H_4 in Titan's atmosphere. Nature 292, 683–686.

McKay, C.P., Coustenis, A., Samuelson, R.E., Lemmon, M.T., Lorenz, R.D., Cabane, M., Rannou, P., Drossart, P., 2001. Physical properties of the organic aerosols and clouds on Titan. Planet. Space Sci. 49, 79–99.

Porco, C., 35 colleagues, 2005. Imaging of Titan from the Cassini spacecraft. Nature 434, 159–168.

Raulin, F., 1987. Organic chemistry in the oceans of Titan. Adv. Space Res. 7 (5), 71–81.

Schulze-Makuch, D., Irwin, L.N., 2004. Life in the Universe: Expectations and Constraints. Springer-Verlag, Berlin/New York.

Simakov, M.B., 2004. Possible biogeochemical cycles on Titan. In: Seckbach, J. (Ed.), Origins: Genesis, Evolution, and Diversity of Life. Kluwer, Dordrecht, pp. 647–665.

Wilson, E.H., Atreya, S.K., 2004. The current state of modeling the photochemistry of Titan's mutually-dependent atmosphere and ionosphere. J. Geophys. Res. 109, doi:10.1029/2003JE002181.