Reports

Ethane Ocean on Titan

Abstract. *It is proposed that Saturn's satellite Titan is covered by an ocean one to several kilometers deep consisting mainly of ethane. If the ocean is in thermodynamic equilibrium with an atmosphere of 3 percent (mole fraction) methane, then its composition is roughly 70 percent ethane, 25 percent methane, and 5 percent nitrogen. Photochemical models predict that ethane is the dominant end product of methane photolysis so that the evolving ocean is both the source and sink for continuing photolysis. The coexisting atmosphere is compatible with Voyager data.*

The Voyager 1 radio occultation experiment placed a probable upper limit on the abundance of methane in the lower atmosphere of Titan of 3 mole percent (*1*), a value well below the 10 percent obtained by assuming the atmosphere to be in equilibrium with a pure CH_4 liquid surface at 94 K. The near-surface temperature gradient inferred from the data is 1.38 ± 0.1 K/km, essentially that of an unsaturated N_2 adiabat over a solid surface. Thus a predominantly CH_4 ocean is very unlikely (*2, 3*). However, the present abundance of CH_4 in the atmosphere will be consumed by photochemical processes in a time on the order of 10^7 years. An almost pure N_2 atmosphere is compatible with the presence of an ocean if the dominant oceanic constituent is less volatile than CH_4 and substantially depresses the CH_4 vapor pressure. Photochemical modeling suggests a natural candidate—ethane. A C_2H_6-rich ocean containing ~ 25 percent CH_4 is not only consistent with the occultation data but also provides a long-lived ($\gtrsim 10^9$ year) source for CH_4 photolysis. The idea of an ocean in which the CH_4 vapor pressure is depressed by the presence of higher hydrocarbons has been suggested independently by Flasar (*2, 4*).

Methane is readily photolyzed in the mesosphere of Titan by absorption of sunlight shortward of 1450 Å to yield the radicals $^1CH_2$, CH_2, and CH, which can react to produce C_2H_4 and C_2H_2 (*5*). The net result can be summarized as

$$2CH_4 \rightarrow C_2H_4 + 2H + H_2$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \text{ (or } H_2 + 4H)$$

With rapid loss of hydrogen by escape, conversion of CH_4 into the heavier hydrogen-poor hydrocarbons is extremely efficient (> 95 percent per CH_4 dissociation) and irreversible. The most likely fate of C_2H_4 in the mesosphere is dissociation to C_2H_2. Since there are no effective permanent sinks for C_2H_2 in the mesophere, the molecule flows down to the stratosphere and is ultimately removed by condensation at the tropopause.

Photochemistry in the stratosphere is initiated by absorption of photons between 1450 and 2000 Å by C_2H_2, resulting in the photosensitized dissociation of CH_4, and ultimately the production of C_2H_6. The net result can be summarized as

$$2CH_4 \rightarrow C_2H_6 + H_2$$

$$2CH_4 \rightarrow C_2H_6 + 2H$$

where C_2H_2 plays the role of a catalyst (*6*). With the formation of C_4H_2 (diacetylene) it is possible to drive the photosensitized dissociation of CH_4 with photons as soft as 2300 Å. Since the solar flux increases drastically from 1450 to 2300 Å, the rate of C_2H_6 production in the atmosphere can be much larger than that of C_2H_2. Once it is formed, C_2H_6 is stable against photolysis in part because of shielding by CH_4 and C_2H_2. Stratospheric C_2H_6 is lost primarily by condensation at the tropopause.

The column-averaged mixing ratios for stratospheric H_2, C_2H_6, C_2H_4, C_2H_2, and C_3H_8 predicted by the model (and compared with observed values shown in parentheses) are, respectively, 2.1×10^{-3} (2×10^{-3}), 1.7×10^{-5} (2×10^{-5}), 3.3×10^{-8} (4×10^{-7}), 4×10^{-6} (2×10^{-6}), and 7.9×10^{-7} (2 to 4×10^{-6}); the predicted values compare favorably with the observed values (*7*). In the

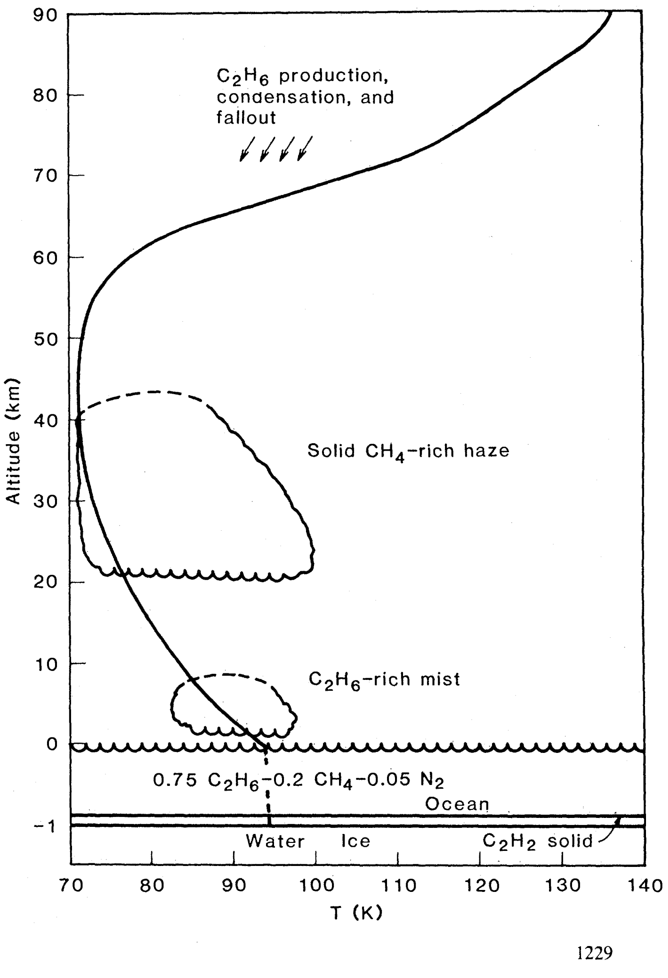

Fig. 1. Model of Titan's near-surface and atmospheric structures. Altitude and temperature data from (*1*). Below surface the temperature in the ocean is assumed to follow an adiabat. Between ~ 10 and 20 km coexisting solid and liquid haze may be present. Note the change in altitude scale below 0 km.

current epoch, CH_4 is being destroyed in the atmosphere at the rate of 1.5×10^{10} cm^{-2} sec^{-1} and converted into C_2H_6, C_2H_2, and C_3H_8 at the rates 5.8×10^9, 1.2×10^9, and 1.4×10^8 cm^{-2} sec^{-1}. The rates of H and H_2 escape from the exosphere are 5.5×10^9 and 7.2×10^9 cm^{-2} sec^{-1}. Over the age of the solar system then, a kilometer-deep primarily ethane liquid surface layer in coexistence with CH_4 and N_2 has accumulated. This depth is compatible with limits derived by Sagan and Dermott (*8*) from a study of the tidal damping of Titan's orbital eccentricity.

Thermodynamic data on the C_2H_6-CH_4-N_2 system is restricted to temperatures above 110 K (*9*); however, there are lower temperature data on the binary end-members of this ternary, and we have estimated equilibrium abundances of the three components for the present conditions at the surface of Titan. In the C_2H_6-CH_4 binary (*10*), the C_2H_6 vapor pressure at 94 K, Titan's surface temperature, is only $\sim 10^{-5}$ bars. If we require the CH_4 mixing ratio at the base of the atmosphere to be constrained between 1.6 and 3 percent, as suggested by Voyager data, then the CH_4 mole fraction of the liquid is between 13 and 25 percent (*11*). To estimate the N_2 content of the ocean, N_2-CH_4 and N_2-C_2H_6 solubility data (*12*) were used to estimate the Henry's law constant for N_2 in the C_2H_6-CH_4 mixture (*13*). Assuming the ternary system to be ideal, we find an N_2 mole fraction in the ocean of $X(N_2) \approx 0.05$ (*14*). The presence of at least several percent propane dissolved in the liquid, as implied by the Voyager data, does not alter substantially the CH_4 and N_2 mixing ratios derived above.

At the present temperature of Titan's surface, C_2H_2 is a solid. We estimate its solubility in the ocean at 94 K to be $\leqslant 3.1 \times 10^{-4}$ (*15*). The ocean floor should be covered with a solid C_2H_2 layer 100 to 200 m thick (*16*) plus a small amount of heavier organic debris (*17*).

We turn now to the atmospheric structure and meteorology above an C_2H_6-CH_4 ocean. A rising parcel of gas, expanding adiabatically, forms C_2H_6-rich droplets and follows a temperature path defined by a "wet" adiabat. Since the relevant vapor pressure is predominantly that of C_2H_6, the resulting lapse rate is found to be about 1.4 K/km, essentially indistinguishable from the dry N_2 adiabat or the radio occultation result of 1.38 ± 0.1 K/km (*1*). This should be contrasted with the expected wet adiabatic lapse rate of 0.6 K/km for a CH_4 ocean (*18*). Despite the small amount of condensation, it is possible to have significant scattering optical depth: the condensation of a few tens of microbars of C_2H_6 into 0.1-μm droplets gives an optical depth in excess of unity. This may affect the radiative-convective transport in the lower atmosphere, which could be relevant to understanding the transition from adiabatic to subadiabatic conditions at 3.5 km, as inferred from the radio occultation data.

At successively higher levels in the atmosphere, droplet condensation still occurs; the composition of the droplets becomes more CH_4-rich, as dictated by the rapidly decreasing C_2H_6 vapor pressure and nearly constant CH_4 gas mixing ratio. At about 80 K, at an altitude of about 15 km, two condensates are formed—a CH_4-rich solid and a very small amount of liquid that grades with decreasing temperature to a eutectic composition of about 35 percent C_2H_6 at 77 K (*19*). This defines the predominant region of CH_4 condensation and haze formation in the troposphere.

The structures of ocean and atmosphere are illustrated in Fig. 1. The ocean contains the equivalent of at least one Titan atmosphere of CH_4, sufficient to maintain photolysis for $\geq 10^9$ years, and at least one-half Titan atmosphere of N_2, a significant buffer of the present atmosphere. The most important observational tests of our model are (i) verification of the presence of CH_4 clouds as an opacity source in the lower atmosphere (*20*); (ii) detection of C_2H_6 saturation or near saturation in the lower troposphere; and (iii) evidence (from radar or other sources) of an essentially global ocean, since the expected depth exceeds nearly all probable elevation differences for an icy satellite such as Ganymede.

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References and Notes

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2. F. M. Flasar, *Science* **221**, 55 (1983).
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4. F. M. Flasar (*2*) and J. Pearl proposed a 50-50 mixture for the ethane-methane ocean as reported in *Science News* [**124**, 28 (1983)].
5. The essential aspects of mesospheric chemistry of CH_4 were described by D. F. Strobel [*J. Atmos. Sci.* **30**, 489 (1973); *Icarus* **21**, 466 (1974)]. Laboratory studies which produced substantial amounts of C_2 and C_3 hydrocarbons from CH_4 dissociation were reported by A. C. Lasaga *et al.* [*Science* **174**, 53 (1971)], T. Scattergood and T. Owen [*Icarus* **30**, 780 (1977)], S. Chang *et al.* [*Rev. Geophys. Space Phys.* **17**, 1923 (1979)], A. Bar-Nun and M. Podolak [*Icarus* **38**, 115 (1979)], and S. Gupta *et al.* [*Nature (London)* **293**, 725 (1981)].
6. The possibility of photosensitized dissociation of CH_4 and subsequent stratospheric chemistry was first proposed by M. Allen, J. P. Pinto, and Y. L. Yung [*Astrophys. J. Lett.* **242**, L125 (1980)]. Recent laboratory investigations of the photochemistry and chemical kinetics of C_2H_2 by H. Okabe [*J. Chem. Phys.* **75**, 2772 (1981); *ibid.* **78**, 1312 (1983)] put the theory of stratospheric chemistry on a solid basis.
7. The complete model is referred to Y. L. Yung, M. Allen, and J. P. Pinto [*Astrophys. J. Suppl. Ser.*, in press]. The column-averaged mixing ratio is defined as the ratio of the column-integrated abundance of a given species to the same column of N_2 above the tropopause. The observations are from Voyager 1 and 2 published data [*Science* **212** (10 April 1981); *Nature (London)* **292** (20 August 1981); *J. Geophys. Res.* **87** (1 March 1982)]. Integrated production rates and fluxes refer to the surface.
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11. If the CH_4 is not perfectly mixed, its surface mixing ratio could be as high as ~ 9 percent (*2*). This yields an ocean with as much as ~ 70 percent CH_4. If the ocean is more CH_4-rich, then it can only be deeper than our estimated 1 km since the total C_2H_6 in the ocean is bounded below by photochemical considerations.
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14. A miscibility gap is possible with an N_2-CH_4 layer separating above a primarily C_2H_6-CH_4 layer (*9*). An approximate extrapolation of the 111 K data down to 94 K, suggests that the miscibility gap requires $X(N_2) \geqslant 0.15$.
15. Calculated from data in J. M. Prausnitz (*13*, p. 385) and G. T. Preston and J. M. Prausnitz [*Ind. Eng. Chem. Process Des. Dev.* **9**, 264 (1970)].
16. The density at 94 K of the liquid mixture is 0.61 g/cm^3 [R. D. Goodwin, H. M. Roder, G. C. Straty, *Nat. Bur. Stand. (U.S.) Tech. Note* **684**, 64 (1976); R. D. Goodwin, *ibid.* **653**, 136 (1974); R. T. Jacobsen and R. B. Stewart, *J. Phys. Chem. Ref. Data* **2**, 757 (1973)]. A density of 0.78 g/cm^3 at 94 K for solid acetylene was extrapolated from R. G. Amamchyan and A. I. Moroz [*Tr. Vses. Nauchno-Issled. Inst. Kislorodn. Mashinostr.* **10**, 150 (1965)].
17. We also examined the solubility of minor constituents in the ocean. The CO_2 is sufficiently soluble that an amount equal to the inferred atmospheric abundance of CO [B. L. Lutz, C. de Bergh, T. Owen, *Science* **220**, 1374 (1983)] may be dissolved. The CO and H_2 are relatively insoluble. Because the ocean is capable of dissolving large amounts of Ar and Kr it will control their atmospheric abundances. The Kr/Ar ratio over the ocean can be predicted and is thus diagnostic of the evolution of Titan.
18. Calculated from a generalized form of an equation described by J. S. Houghton [*Physics of Atmospheres* (Cambridge Univ. Press, Cambridge, 1977), p. 19]. G. F. Lindal *et al.* (*1*), in computing the saturated adiabat for CH_4, used an expression that omitted a term involving the change of vapor pressure with temperature and hence found a value of 0.3 K/km.
19. The temperature and composition at which the solid-liquid boundary is crossed depends on the surface CH_4 mole fraction, assumed to be 3 percent. Eutectic composition estimated from F. Pavese [*J. Chem. Thermodyn.* **10**, 369 (1978)] and other data (*15*).
20. Models that support the presence of methane clouds are those of R. Courtin [*Icarus* **51**, 466 (1982)] and R. E. Samuelson [*ibid.* **53**, 364 (1983)].
21. We thank J. Pearl, D. M. Hunten, and C. Sagan for helpful discussions and R. E. Samuelson and F. M. Flasar for detailed reviews of the manuscript. Supported by NASA grants NSG 7376 and NAGW 185. Contribution number 3933 from the Division of Geological and Planetary Sciences, California Institute of Technology.

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