

2.12 ORGANIC CHEMISTRY IN THE ATMOSPHERE

C. Sagan

Introduction

There seems little doubt about the existence of an at least moderately complex organic chemistry on Titan. There is clear evidence of methane, and at least presumptive evidence of hydrogen in the atmosphere. The ratio of methane to hydrogen is the highest of any atmosphere in the solar system. The irradiation of methane/hydrogen mixtures is well-known to produce aromatic and aliphatic hydrocarbons. In addition, we know that Titan is cloud-covered and that the clouds are red. A very reasonable hypothesis is that the clouds are made of organic chemicals. I want in this paper to describe some experimental work which bears upon the possible organic chemistry of the Titanian environment.

Titan Organic Chemistry

First, suppose we have a mixture of the fully saturated hydrides of the cosmically most abundant reactive elements, hydrogen, oxygen, nitrogen and carbon. If we irradiate this mixture of methane, ammonia, water and hydrogen with short wavelength ultraviolet light -- or if we spark it in an electrical discharge, or indeed if we supply energy in any way which produces free radicals which can recombine at lower temperatures -- we produce the following simple organic compounds: the simple two carbon hydrocarbons, ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2); the simplest nitriles, hydrocyanic acid (HCN) and acetonitrile (CH_3CN); and, in the presence of water, the simplest aldehydes, formaldehyde (HCHO) and acetaldehyde (CH_3CHO). Carbon monoxide is also produced. The abundance of C_2 compounds in these experiments is variable but characteristically ranges from 10^{-2} to 10^{-6} by number, compared with the initial CH_4 . These compounds are formed in experiments in which there is a great excess of hydrogen to other constituents, as well as in experiments in which the precursors are present in approximately equimolar quantities. Such experiments are characteristically performed at pressures ranging from a few tenths of a bar to 1 bar, and at temperatures from room temperature to $77^\circ K$. There does not appear to be a striking dependence of the results on the starting temperatures and pressures. In addition, all such experiments are performed in glass vessels -- but if there are wall effects, silicates are not unlikely catalysts in a planetary environment. These results are also obtained in computer quenched thermodynamic equilibrium experiments. Although the solar flux is down by a factor of 100 at Titan compared to the Earth, the ultraviolet irradiation dose may still be significant. In addition, electrical discharges in the Titanian clouds are to be expected. Therefore adequate energy sources probably exist in Titan. Also of interest is the fact that -- except for the hydrocarbons which have no permitted microwave lines -- all of the above molecules are found in the interstellar medium by radioastronomical line experiments.

Consequently there seems nothing very daring in proposing two-carbon hydrocarbons in the upper atmosphere of Titan. At lower depths, if ammonia is present, nitriles can be expected. If the surface temperatures on Titan are high enough

to permit a significant vapor pressure of water vapor, aldehydes might also exist in the lower atmosphere. But these compounds are not the stable end products of the photochemistry of the Titanian atmosphere and we must inquire further about larger molecules.

Laboratory Simulation Experiments

There are of course no color photographs of Titan but the color of Titan and Saturn are not very different, and color photographs of Saturn are well-known to show a range of yellows, oranges, browns and reds. That polymeric material with such colors is readily produced under simulated Saturnian or Titanian conditions is a simple consequence of the appropriate simulation experiments. Figure 2-44 shows a characteristic experimental design from our Laboratory, in which a reaction vessel filled with precursor gases is irradiated in cylindrical geometry by the 2537 Å and in some experiments also by the 1849 Å line of mercury. The reactants are circulated Hg-free by a greaseless solenoid pump through a liquid water bath (more precisely, a NH_4OH bath) and then back again to the reaction vessel. Because hydrogen, methane, ammonia and water are all transparent at 2537 Å, these experiments use either H_2S or HCHO as the initial photon acceptor. The initial photodissociation event produces a hot hydrogen atom which is a few electron volts superthermal, and which initiates chain reactions in collision with other gases. Similar results are obtained, for example, by electrical discharges or shocks in essentially the same manner -- by producing free radicals. These particular experiments were designed to utilize the longest possible wavelengths of ultraviolet light, but any other energy source which produces free radicals should yield essentially similar results. We are at the present time engaged in experiments which more precisely simulate Titanian conditions.

Simulation Products

After a few days the reaction vessel becomes entirely coated with a reddish brown polymeric material, of which a color photograph has been published (Sagan 1971). The polymer is a flaky powder of typical particle size about 100 μm , which, on acid hydrolysis, yields a very substantial harvest of protein and non-protein amino acids. From this polymer we have isolated some 40 or 50 ninhydrin-positive peaks on the automated amino acid analyzer -- almost all of which are amino acids. We have made the first prebiological organic synthesis of the sulfur-containing amino acid cystine in such experiments. Either polynitriles are produced, which, upon solution in liquid water, give amino acids through the Strecker synthesis; or polypeptides -- polymers of amino acids -- are produced directly and hydrolyzed under acid hydrolysis.

The amino acid yields in these experiments are enormous. A good way of characterizing them is to ask what column density of amino acids would be produced after 10^9 years of ultraviolet irradiation on the primitive Earth. The answer is about 200 kg cm^{-2} , which is more than the carbon content of the sedimentary column. This simply means that amino acids are destroyed as well as made. When amino acid destruction at typical terrestrial temperatures is included, the result corresponds to about 1 kg cm^{-2} in 10^9 years, or approximately a 1 percent solution of organic compounds of amino acids in the primitive oceans. On Titan the thermal degradation of amino acids should be much slower, and probably slow enough to compensate for the factor of 100 lower ultraviolet flux.

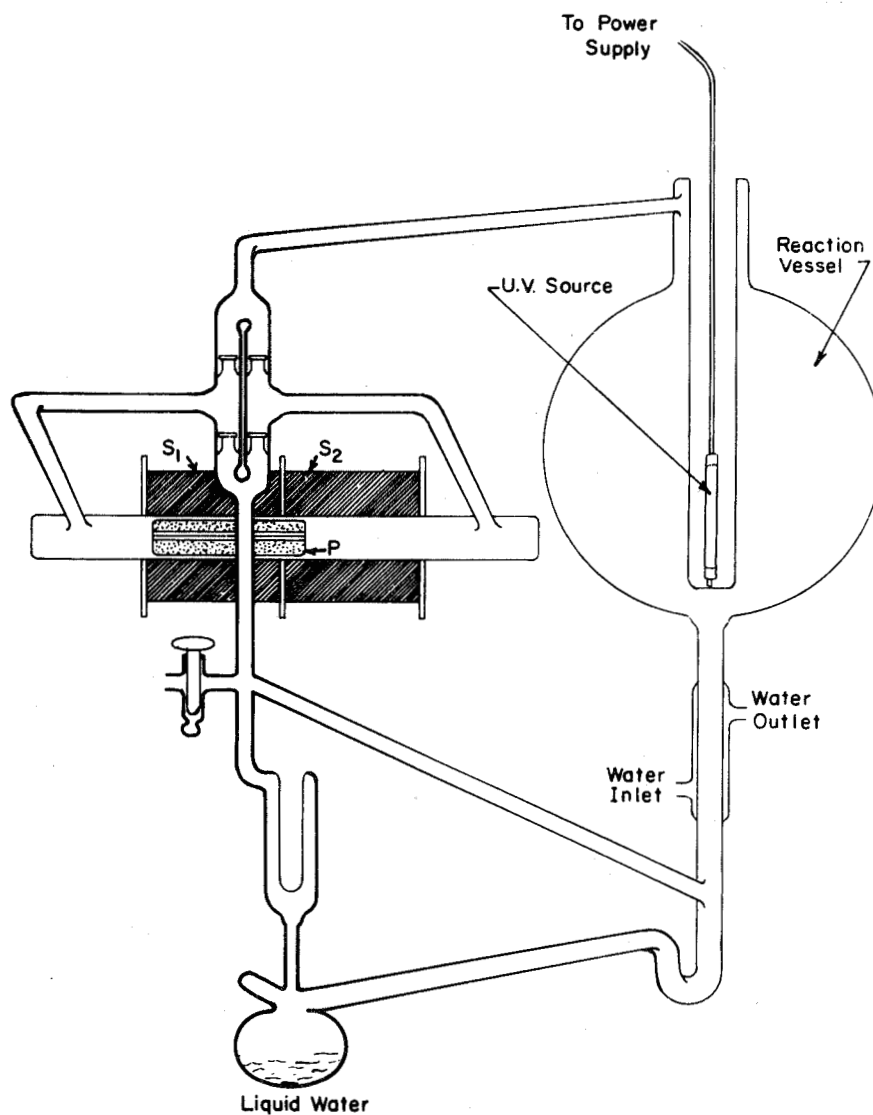


Figure 2-44. Schematic illustration of the ultraviolet organic synthetic experiment at Cornell University. After Khare and Sagan (1973). Reprinted from *Icarus*, 20:in press, with permission of Academic Press, Inc. All rights reserved.

Dr. Khare and I have examined the brownish polymer by ultraviolet, visible, and infrared spectroscopy, gas chromatography and mass spectrometry. The preliminary results are that the principal constituent is a long straight-chain hydrocarbon -- an alkane. While polymeric sulfur is made in the aqueous solution it is not a principal constituent of the brown polymer. As far as we can tell, the major chromophores are hydrocarbons. The polymer also contains carbonyl and amino groups, but they do not contribute significantly to the coloration.

Polymeric Transmission Spectra

In Figure 2-45 is the ultraviolet and visible transmission spectrum of the brown polymer. This is a double-beam analysis in which a fragment of the vessel coated with polymer has its transmission spectrum automatically compared with a comparable fragment of a similar reaction vessel without the polymer coating. You can see the very sharp decline in transmission from yellow to ultraviolet, giving this material its reddish coloration. At long visible wavelengths, the transmission is moderately constant. At short optical frequencies the transmission corresponds to something like λ^{-4} and the optical depth to λ^{-2} . There is no reason to think that this is the reddest material that can be produced under these conditions; and indeed we have succeeded in separating via paper chromatography a yellow component of this polymer which runs with the solvent front. This material appears to be substantially redder than the parent brown polymer. I would not at all be surprised if materials with optical depth proportional to λ^{-3} or λ^{-4} are easy to come by in such experiments.

As I've mentioned, the particle size in these experiments is something like 100 μm with a dispersion of a factor of 3 or 4 or 5. The particle sizes are certainly determined in part by wall effects and by the time of irradiation, and I do not know to what extent the 100 μm particle size is characteristic of Titanian conditions. However the results do suggest some caution in concluding that the particles produced in the Titanian clouds must be smaller in diameter than the near infrared wavelengths.

The ultraviolet absorption coefficient is fairly large, about 10^3 cm^{-1} in the near ultraviolet -- which means that a single 100 μm particle has an optical depth in the ultraviolet of about 0.1. It's a pretty sizable absorber. You don't need a lot of this material in order to produce the kinds of optical depths that are talked about in models of the clouds of Titan. Therefore it is entirely possible to imagine a situation in which materials such as this polymer are being made on Titan, fall out in accordance with the Stokes-Cunningham equation, and are replaced by further production -- so that the steady-state abundance is adequate for all optical properties of the clouds.

In Figure 2-46 is an infrared transmission spectrum of two polymeric components -- I is the full brown polymer, and II the yellow chromatographic fraction which I referred to above. There are a number of points of interest: one is the enormous absorption feature at 3 μm which is due to the C-H stretch of the hydrocarbons which are the primary constituent of the polymer.

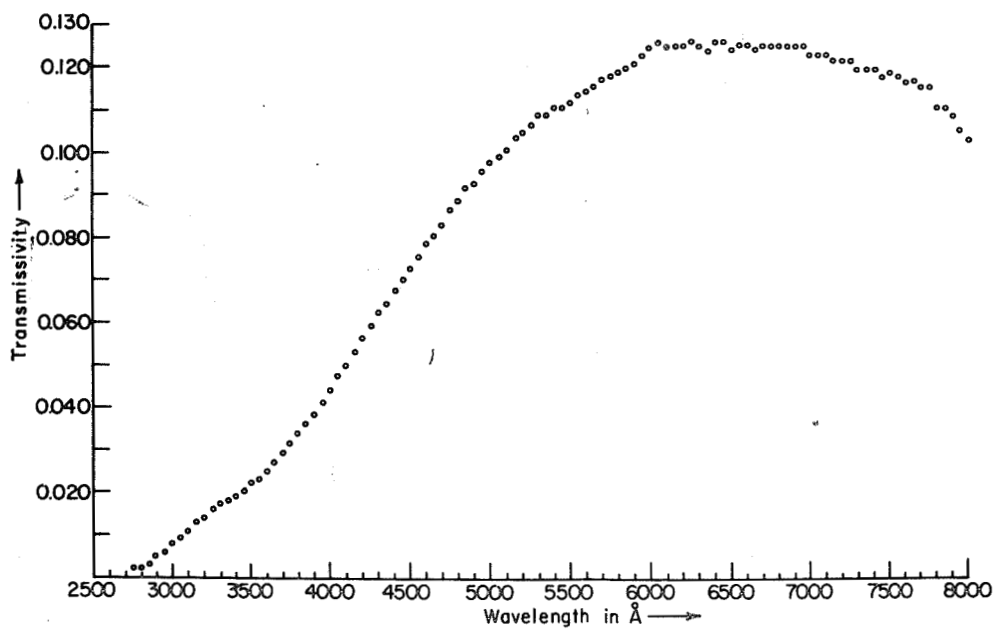


Figure 2-45. Visible and near-UV transmission spectrum of the brown ultra-violet polymer. The spectrum was obtained on a double-beam spectrometer against a glass sample undercoated by polymer. After Khare and Sagan (1973). Reprinted from *Icarus*, 20:in press, with permission of Academic Press, Inc. All rights reserved.

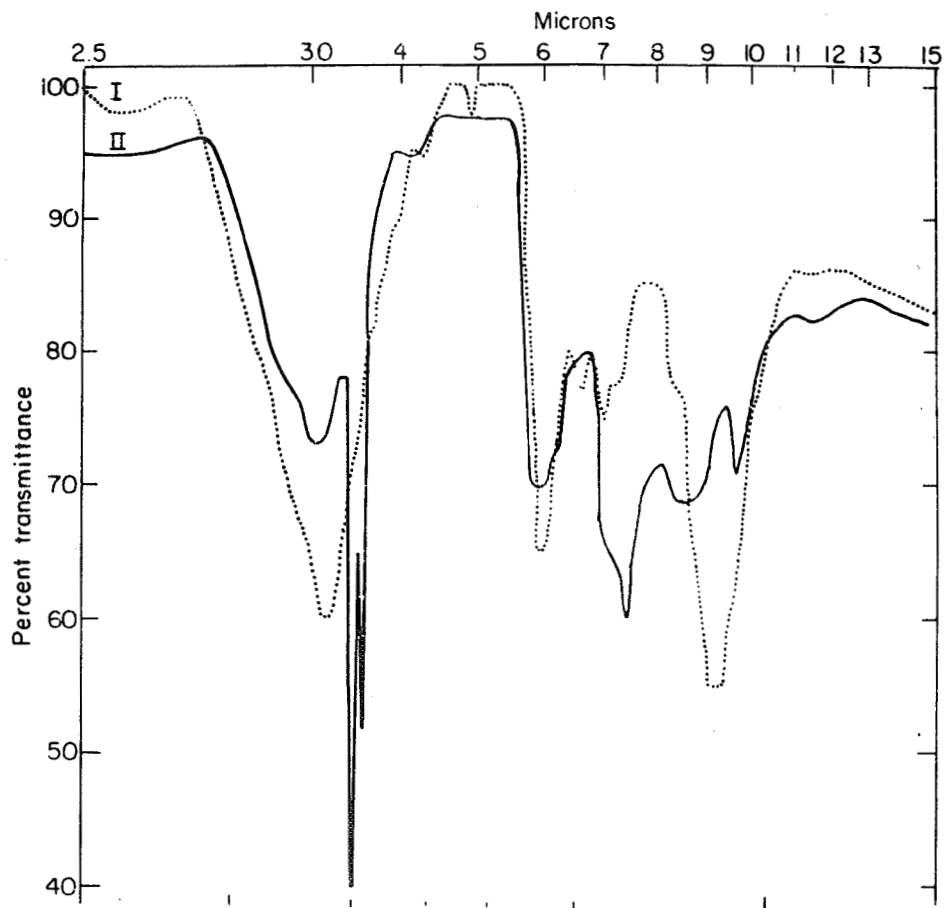


Figure 2-46. Infrared transmission spectrum of the brown polymer and the yellow-chromatographic fraction of this polymer. After Khare and Sagan (1973). Reprinted from *Icarus*, 20:in press, with permission of Academic Press, Inc. All rights reserved.

Next there is substantial and complex absorption in the 7-11 micron region. Therefore it is conceivable that some of the observed absorption features in the 8-13 micron region are due, not to atmospheric emission, but to aerosol absorption. It is also reasonable that the clouds have substantial opacity at 10 μm and that therefore we are not seeing to the surface at such wavelengths.

Another point of interest has to do with the 5-micron window. In material of this sort, the characteristic absorber near 5 μm is the nitrile group, CN. The fact that we are reasonably transparent at these wavelengths means that we are not producing a great many polynitriles. In work by Cyril Ponnampetura in which his starting materials were ammonia and HCN, he did produce a large quantity of polynitriles and his infrared transmission spectra did show a great deal of absorption at 5 μm . This is of course a reflection of his starting conditions: nitriles in, nitriles out. The results suggest that the examination of the infrared spectrum of such clouds might give some information on the starting conditions.

If our infrared spectrum (Figure 2-46) is typical of the Titanian clouds, then we might see substantially deep into the atmosphere at 5 μm , and experiments of this sort recently reported in a preliminary way by Owen are well worth following up. There is of course multiple scattering in the clouds and even a very large single scattering albedo may imply a small penetration of infrared light through the clouds. But this is true at all infrared wavelengths and the fact that the opacity is lowest in the vicinity of 5 μm suggests that this should be a particularly important wavelength for infrared radiometry. At infrared wavelengths longer than 15 μm I have the impression that there are not a large number of interesting absorption features, but we are still studying this region.

I have talked about very simple products, with as few as three to six atoms, and very complex polymeric material. What about material of intermediate complexity? We do not yet have a good handle on this. We go from simple to complex molecules so fast in such experiments that we are left breathless. Just to give an idea: suppose we take a simple mass spectrum of the polymeric material. We find that every mass-to-charge number from 1 to 1000 is occupied. The complexity of the material is striking.

I have not mentioned much about the chemistry of the aqueous phase in these experiments because there is still a substantial question of whether ammonia hydroxide oceans can exist on Titan. But the organic chemistry in such a liquid medium is of considerable interest.

Conclusions

There is a tradition in astronomy of extreme caution on the question of biology on this or that planet. I believe that Titan looks biologically very promising. There might be as serious an error in being prematurely over-cautious as in being prematurely over-enthusiastic. I do not think we would be doing any disservice if we said that the planning of exobiological experiments on Titan makes some sense. However, even in the absence of any biology on Titan, the presence of interesting organic chemistry -- possibly related to the origin of life on Earth -- looks so promising that I think substantial support from the

biological community could be forthcoming in planning, for example, gas chromatograph/mass spectrometer entry probes into the Titanian atmosphere. Apart from the Viking GC/MS which is intended as a post-landing experiment, the gas chromatograph being planned for Venus Pioneer entry probes might be an appropriate precursor instrument.

While the relative hydrogen abundance elsewhere is greater than on Titan, it also seems possible that the Titanian organic chemistry is characteristic of that of the outer solar system in general. Since Titan is the easiest body with an atmosphere to enter in the outer solar system, the exploration of Titan may be the primary stage in the study of the organic chemistry of the entire outer solar system.

Acknowledgement

The recent experimental work reported here has been done jointly with Dr. B. N. Khare, and will be published shortly (Khare and Sagan Icarus, 20). This paper was supported by NASA/JPL Grant NGR 33-010-101.

Pollack: In discussing the laboratory experiments, did you imply that the aldehydes were produced in passing through liquid water?

Sagan: The initial experiments were all in the gaseous phase. However, if a somewhat artificial experiment was performed whereby the products from photolysis or pyrolysis of methane, ammonia and hydrogen were formed in the absence of water vapor, but were then carried into liquid water, the results would be similar. The experiment shown in Figure 2-44 has water in both the vapor and liquid phases.

Danielson: Am I right in saying that you use H₂S as an experimental convenience or are you simulating a Titanian atmosphere?

Sagan: Although there has been some discussion of the possibility of H₂S in the atmospheres of the Jovian planets, and indeed the cosmic abundance of sulfur is high, we have used H₂S as a convenient laboratory source for hot hydrogen atoms. I should stress that none of the color effects which we see in the brown coating are due to polymeric sulfur.

Blamont: I would be happy to provide you with a Lyman- α source which would fit inside your experiment.

Sagan: Thank you; that would be excellent. To substitute Lyman- α excitation for H₂S would be very useful.