

stant of the PSB during the photocycle. Among many other facets of the bR structure and function that need to be understood are the details of the proton movement that leads to the creation of the proton gradients.

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Titan: A Laboratory for Prebiological Organic Chemistry

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Introduction

While the presence of complex kerogen-like organic solids in some meteorites has been recognized since the time of Berzelius, a general understanding that organic molecules are pervasive in the solar system has been slow in achieving consensus in the astronomical community. In part this has been due to the fact that the inner solar system in which the Earth is embedded is not in a reducing oxidation state. But when we examine the atmospheres of the Jovian planets (Jupiter, Saturn, Uranus, and Neptune), the satellites in the outer solar system, comets, and even—through microwave and infrared spectroscopy—the cold dilute gas and grains between the stars, we find a rich organic chemistry, presumably abiological, not only in most of the solar system but throughout the Milky Way galaxy. In part because the composition and surface pressure of the Earth's atmosphere 4×10^9 years ago are unknown, laboratory experiments on prebiological organic chemistry are at best suggestive; but we can test our understanding by looking more closely at the observed extraterrestrial organic chemistry. The present Account is restricted to atmospheric organic chemistry, primarily on the large moon of Saturn.

Titan is a test of our understanding of the organic chemistry of planetary atmospheres. Its atmospheric bulk composition (N_2/CH_4) is intermediate between the highly reducing ($H_2/He/CH_4/NH_3/H_2O$) atmospheres of the Jovian planets and the more oxidized ($N_2/CO_2/H_2O$) atmospheres of the terrestrial planets Mars

and Venus. It has long been recognized¹ that Titan's organic chemistry may have some relevance to the events that led to the origin of life on Earth. But with Titan surface temperatures ≈ 94 K and pressures ≈ 1.6 bar, the oceans of the early Earth have no ready analogue on Titan. Nevertheless, tectonic events in the water ice-rich interior² or impact melting and slow re-freezing³ may lead to an episodic availability of liquid water. Indeed, the latter process is the equivalent of a $\sim 10^3$ -year-duration shallow aqueous sea over the entire surface of Titan.

When the Voyager 1 and Voyager 2 spacecraft flew by Titan in 1980 and 1981, the cameras uncovered an enveloping pinkish-orange haze layer unbroken even at kilometer resolution. Through differential refraction, a radio-occultation experiment determined the atmospheric structure from high above the visible haze down to the surface. The atmospheric chemistry was examined⁴ by an infrared interferometric spectrometer (IRIS). Six simple gas-phase hydrocarbons ($HC\equiv CH$, $H_2C=CH_2$, H_3CCH_3 , $H_3CCH_2CH_3$, $H_3CC=CH$, $HC\equiv CC=CH$) and three nitriles ($HC\equiv N$, $N\equiv CC\equiv N$, $HC\equiv CC\equiv N$) were found. Stratospheric volume mixing ratios for these compounds varied from the 10 ppm range for ethane down to the 1–10 ppb range for C_3H_4 , C_4H_2 , HC_3N , and C_2N_2 . The pole-to-equator abundance ratios range from ~ 1 for the C_2 -hydrocarbons to ~ 10 –100. The observations are summarized (E for equatorial abundances, P for polar) in Figure 1. One important question, posed by Voyager, is why these minor organic constituents and not others are prominently produced from the major constituents (N_2 and CH_4) in the atmosphere of Titan.

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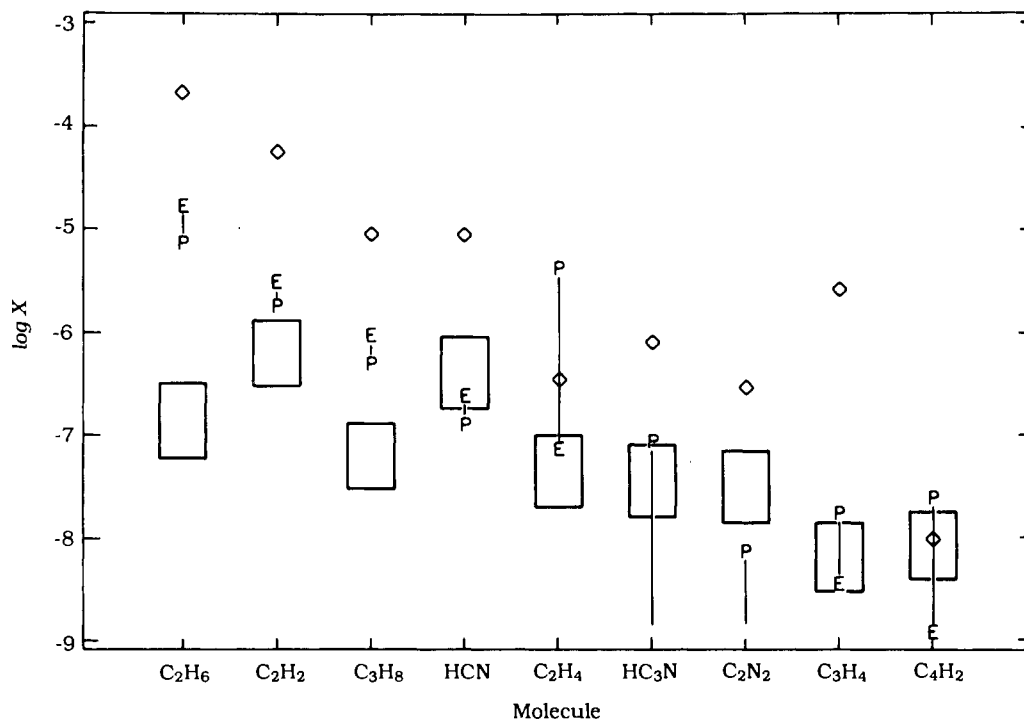


Figure 1. Comparison of the mole fraction range computed from¹³ laboratory plus eddy mixing model (large rectangles) and mole fractions computed by photochemical kinetics read from the figures of ref 10 (diamonds) with the Voyager IRIS-derived values determined for Titan's equatorial (ref 31) and polar (ref 32) regions. The equatorial and polar mole fractions are marked, respectively, by the letters E and P and are connected by a tie line to indicate the equatorial to polar range.

Among the prominent pre-Voyager ground-based discoveries about Titan were (1) the presence of a methane-rich atmosphere⁵ (any atmosphere was initially surprising for a lunar-sized body, but it is readily explicable by the low temperature of the exosphere, the level from which escape to space occurs) and (2) the satellite's reddish color⁶ (which was initially attributed to a prominent UV electronic transition of surface rocks spilling over into the visible). More puzzling were (3) measurements of the polarization of (initially unpolarized) sunlight reflected off Titan as a function of the phase angle, Sun-Titan-Earth; the absence of a negative branch at small phase angles implies that we are viewing not a solid surface, but rather an opaque aerosol haze or cloud layer surmounted by a thin Rayleigh atmosphere.⁷ This trio of ground-based measurements and deductions led (in 1974) to the suggestion¹ that the aerosols are organic solids generated by the irradiation of the principal atmospheric constituents, and that gas-phase organics should be produced by the same processes. By measuring reflected sunlight and emitted thermal radiation as a function of the phase angle Sun-Titan-spacecraft, Voyagers 1 and 2 were able to determine the optical constants (the real and imaginary parts of the complex refractive index) and particle sizes of the upper atmospheric aerosols on Titan through Mie light scattering theory.⁸ Another important question, posed by these ground-based and spacecraft observations, is the composition of the Titan aerosols and how they are generated.

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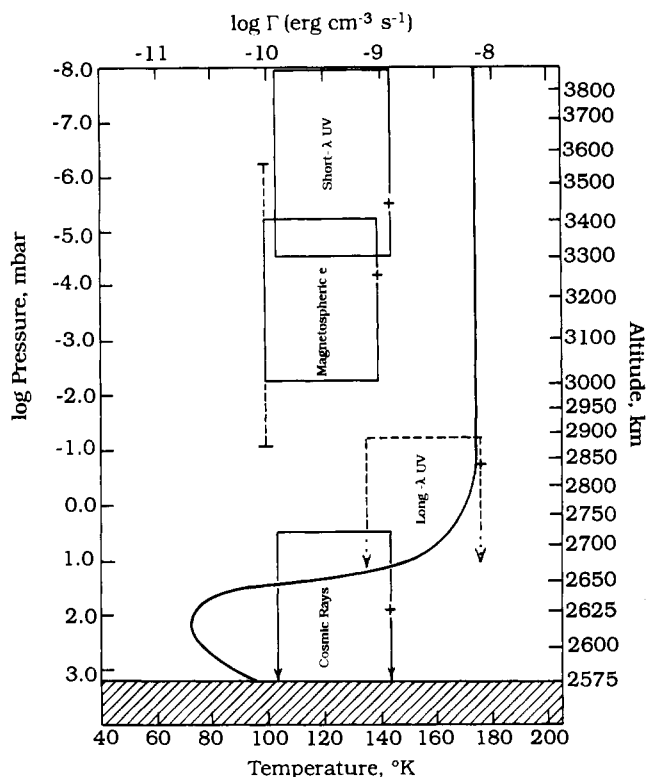


Figure 2. Energy deposition regimes in Titan's atmosphere, Γ , as a function of altitude, r , from the center of Titan and, equivalently, of atmospheric pressure, P . Also displayed is the atmospheric structure profile, $T(r, P)$. Altitudes of maximum energy deposition are indicated by "+"; altitudes over which the various energy sources are within 1 order of magnitude of their peak values are indicated by the boxes. The dashed lines indicate altitudes at which Γ is within 2 orders of magnitude of peak values. Titan's surface is shown hatched at the bottom.

Estimates—based on Voyager data—of the power dissipated per unit volume of atmosphere by the various

sources of available radiation deposited on Titan as a function of altitude are shown in Figure 2 (cf. ref 9). Short-wave solar ultraviolet light is mainly absorbed by N_2 and CH_4 at high altitudes, solar and galactic cosmic rays near the surface, and long-wave solar UV radiation at intermediate altitudes. Titan sits, for most of its orbit, within the trapped radiation belts of Saturn. The high-energy tail of the Saturnian magnetospheric electron flux is a significant source of energy deposition in the stratosphere of Titan (above the optically thick regime of the atmosphere, which begins at about the 30-mbar level). A Voyager-derived profile of the atmospheric structure is also displayed in Figure 2.

Knowledge of radiation deposition rates at various depths in the atmosphere permits both theoretical and experimental simulations of Titan's atmospheric chemistry to be attempted. Gas-phase chemistry has been simulated by absolute reaction rate photochemical kinetics, beginning with UV photodissociation of methane in Titan's upper atmosphere.¹⁰ The results are compared with observations in Figure 1; in most cases, the predicted abundances are 1–2 orders of magnitude larger than the observations. The reason for this discrepancy is unknown. No plausible conclusions, consistent with the measured optical constants, on the identity of the Titan aerosols have emerged from kinetics modeling.

Early Experimental Simulations

It has taken a long time for even barely adequate laboratory techniques to be applied to the chemistry of reducing planetary atmospheres. Simulation attempts have been almost entirely in the hands of planetary scientists with only a little help from professional chemists, which helps account for how slowly this sequence of successive approximations has progressed.

In the first simulation of the atmosphere of another planet,¹¹ performed in 1958–1959, a 10:1:0.3 mixture of $H_2/CH_4/NH_3$ was sparked with a Tesla coil at $T \approx 300$ K and $p \approx 1$ bar, in a crude simulation of the deepest levels accessible to observation in the atmosphere of Jupiter. However, the hydrogen dilution was too low by a factor of 100, product molecules were repeatedly subjected to the spark (leading to secondary processing of the primary products), and wall effects may have been important. Unsaturated ($H_2C=CH_2$, $HC\equiv CH$) and saturated (H_3CCH_3) hydrocarbons, as well as nitriles ($HC\equiv N$, $CH_3C\equiv N$), were generated; and each of these products, except the last, has since been discovered spectroscopically in the Jovian atmosphere.

In such experiments, in addition to gas-phase organic products, complex brownish powdery or sticky organic solids are always generated, usually on the walls of the reaction vessel and in low-temperature traps downstream of the energy source. In general, the precursors are not pure hydrocarbons, and neither are the solid products. They have been called "intractable polymers", but as we outline below, they are not wholly intractable. They are also, in general, not polymers: not simple repetitions of the same monomer. We have therefore proposed¹² the model-independent term

"tholins", from the Greek word for "muddy".

Only in the last few years have simulation experiments approached a minimum acceptable set of conditions which might justify their being taken seriously, viz., that they

1. employ starting compositions and energy sources known to apply to the atmosphere being simulated;
2. be run at pressures and temperatures appropriate to the energy sources and atmospheric depths being simulated;
3. have mean free paths much less than the dimensions of the reaction vessel (to minimize wall effects); and
4. have low power:mass ratios, so only primary product yields are measured (to minimize unrealistic secondary processing).

Gas-Phase Radiation Chemistry Simulations for Titan

We now describe a recent set of experiments in simulated high altitudes of Titan's atmosphere.¹³ They represent the most successful simulations to date, but still have some deficiencies. We hope that chemists not now working on solar system problems might be tempted to help improve the state of the art.

In these experiments, a glow discharge is employed, which is a plasma characterized by an approximately Maxwellian electron energy spectrum with $\langle E \rangle = 1\text{--}10$ eV. The electron temperature in this type of plasma is always much greater than the temperature of the gas. In our experiments the continuous flow further ensures that the gas is essentially at room temperature; hence the term cold plasma. Initial ionization events are produced¹⁴ by the high-energy tail of the energy distribution $N(E) \propto E^{1/2} \exp(-E/\langle E \rangle)$. The precipitating magnetospheric electrons at Titan have much higher energies, but it is well-known that the source of initial charged-particle-induced ionization usually has only minor effects on the resulting chemistry. In particular, this is known¹⁵ to be true for CH_4 , where differences in experimental results are due mainly to the loss of reactive species to secondary reactions,¹⁶ which are minimized in the present experiments by low conversion, continuous flow, and cold trapping.

This insensitivity to charged-particle energy may be understood by considering the importance of secondary processes in a high-energy particle track.¹⁷ For a 1-MeV electron, 67% of the total energy is deposited in isolated spurs (spots) along the track, and 22% is deposited in overlapping spurs or short tracks (both characterized by an internal electron energy of $\sim 10\text{--}25$ eV); the remaining 11% is deposited in blobs near the end of the particle track characterized by electron energies of 100–200 eV. A detailed study¹⁸ of the sec-

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ondary electron energy spectrum resulting from 0.57-MeV (^{64}Cu) electrons shows that most of the flux is concentrated around 20 eV. Ionization by γ rays is mostly produced by Compton-scattered electrons; the analogy to electron irradiation follows. The greatest difference is probably expected for nuclear particles, which tend to produce denser, overlapping tracks. But even in that case the results are often similar or identical^{15,16} to those found for other processes. Over half the energy deriving from a 5-MeV α particle is actually deposited by secondary electrons.¹⁸

An inductive cold plasma is a good analogy to energetic charged particle chemistry because (1) the ionizing component of the plasma electrons has energies of order 10 eV, equivalent to those found in $\sim 90\%$ of the spurs along a high-energy electron trail, and (2) as in a planetary stratosphere, the gas is not thermally excited by the radiation. We distinguish this method from electric sparks and shock waves, in which the fundamental processes are quite different.¹⁴

These continuous-flow low-pressure plasma-discharge Titan experiments¹³ were performed on 9:1 N_2/CH_4 atmospheres, simulating the deposition of auroral electrons from the Saturnian magnetosphere onto Titan and (more crudely) the cosmic ray flux there. Unlike the case for most of the solar UV radiation, auroral electrons are readily able to dissociate N_2 .

After a number of preliminary runs in which techniques were tested and improved, experiments were performed at two pressure-level simulations: one at 17 mbar for 49.6 h with 4100 L irradiated at a delivered power of about 0.5 W; the other at 0.24 mbar for 49.3 h with 4900 L irradiated at a delivered power of about 0.04 W. Product analysis was by GC/MS, and yields were quantified by separate continuous flow irradiation experiments using C_2H_4 as a calibration standard. At the higher pressure, corresponding to cosmic ray irradiation of the Titan troposphere, 62 gas-phase species were identified, including 27 nitriles, at a net radiation yield, G , of heavy atoms incorporated into products of 4.0 (C + N)/heV (1 heV = 100 eV). The hydrocarbons were notably saturated. Among the wide variety of products, those of highest molecular mass, produced at $G < 10^{-5}$ molecules/heV, include 2,4-pentadienenitrile, several pentenenitrile isomers, 2-methylene-3-butenitrile, and 1,2,4,5-tetrazine, up to (C + N) = 8. The most abundant products in this 17-mbar experiment do not provide an adequate explanation of the minor constituents detected by Voyager in the Titan atmosphere.

At the lower pressure, 0.24 mbar, corresponding to ~ 1 -MeV Saturnian auroral electrons penetrating deep into the Titan stratosphere, fewer gas-phase species were identified: nine hydrocarbons, six nitriles, and three other incompletely identified N-bearing compounds (possibly including the ring molecule tetrazole). The net yield was 0.79 (C + N)/heV, and the hydrocarbons were largely unsaturated. The decline of abundance with (C + N) number at 0.24 mbar tends to be shallow for unsaturated species and steep for saturated species. If the trend continues, the most complex products would be expected to be the most unsaturated.

To apply these experimental results to Titan, we adopt a simple eddy diffusion model, in which molecules are produced at high altitudes, mix downward through several atmospheric scale heights, and are removed by condensation near the tropopause at altitudes below about 10 mbar (cf. Figure 2). Specifically, the eddy diffusion coefficient scales as $K = K_0(\rho/\rho_0)^{-1/2}$, where ρ is the atmospheric mass density; the steady-state column density of molecular species i is $N_i = 4H^2\phi_i/K_0$, where the atmospheric scale height $H = RT/\mu g$ (with R = universal gas constant, T = temperature, μ = mean molecular mass, and g = local acceleration of gravity), K_0 is the eddy diffusion coefficient at the base of the layer (i.e., at the condensation level for these gases), and $\phi_i = FG_i$ is the production flux of species i for total energy flux F and production efficiency G_i . The mole fraction of species i is $X_i = N_i/N_{\text{tot}}$, where N_{tot} is the total column density of gas above the condensation level. The results are convolved with an altitude integration of the Saturn magnetospheric electron deposition flux at Titan to estimate the column densities and volume mixing ratios of charged particle radiation products in Titan's upper atmosphere, and can then be compared with the Voyager IRIS observations.

Results for the most abundant products in the 0.24-mbar experiments are given in Figure 2. On Titan, C_2H_6 and C_3H_8 derive primarily from UV photolysis of CH_4 , and their abundances are not expected to agree well with the results of charged particle irradiation simulation experiments. For the remaining species, simulation experiments do generally better than absolute reaction rate photochemical kinetics models. Every gas-phase organic found by Voyager is detected in the simulation; they constitute the products generated in highest yield. No additional products are predicted from these experiments at mole fractions detectable by Voyager. As a prod for future, more sensitive, remote or in situ observations, the molecules $\text{CH}_3\text{C}\equiv\text{N}$, $\text{C}-\text{H}_2=\text{CHCH}=\text{CH}_2$, $\text{CH}_2=\text{C}=\text{CH}_2$, and $\text{CH}_2=\text{CHC}\equiv\text{CH}$ are predicted at $X > 10^{-9}$, and $\text{CH}_2=\text{CHC}\equiv\text{N}$, $\text{CH}_3\text{CH}=\text{CH}_2$, and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$ at $X > 10^{-10}$. These results, we suggest, indicate that properly conducted laboratory experiments can now usefully simulate the organic chemistry in planetary atmospheres.

Laboratory Simulations and Kinetic Modeling

Photochemical kinetics remains a useful and relevant technique for understanding simple hydrocarbons in planetary atmospheres. For N-containing and/or more complex molecules a number of drawbacks are evident:

1. Inherently, charge-particle processes, especially local plasma processes, cannot be modeled by conventional purely photochemical kinetics (although complete chemical kinetics models, including both processes, could in principle be constructed).
2. Because of the N_2 bond strength, N_2 photochemistry requires $\lambda \lesssim 90$ nm, and because of the comparatively low solar UV flux at short wavelengths, the relative importance of charged-particle chemistry is greater for N_2 -rich atmospheres.
3. The number of reaction pathways increases steeply, nearly factorially, with the "heavy" atom number (number of atoms with >1 amu), so errors can propagate disastrously if a reaction is

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overlooked or unmodeled, or if a measured rate constant is in error.

- Current computational limits are reached at $\sim 4-6$ (C + N, "heavy") atoms, depending on the sophistication of the models (although some chain reactions—those forming, e.g., polyacetylenes—can be managed).

On the other hand, much more light is cast on the complex branched tree of reactions in the atmosphere of Titan by kinetic modeling than by the experimental results just outlined. Clearly, both laboratory determinations of primary product yields and chemical kinetics models have their own advantages and limitations. There is much to be learned by carefully designed and coordinated attacks on model precursor gas mixtures by chemical kinetics models and laboratory simulation experiments working together.

Titan Tholins

In a continuing series of experiments in this laboratory, in cooperation with E. T. Arakawa of Oak Ridge National Laboratory, the real (n) and imaginary (k) parts of the complex refractive index of Titan tholin, the brownish solid produced in simulations like those just described, have been measured from soft X-rays to microwaves¹⁹ through a combination of transmittance, specular reflectance, interferometric, Brewster angle, and ellipsometric polarization measurements. The experimental uncertainties in n are estimated to be ± 0.05 , and in k , $\pm 30\%$. At $\lambda < 550$ nm, short of the Kuiper CH₄ bands, simple radiative-transfer theory and a monodisperse size distribution function showed reasonable agreement of Titan tholin with the ground-based and Earth-orbital reflectance spectrum of Titan (refs 21 and 22 and Figure 3). Much more sophisticated analysis now predicts the optical constants necessary for a polydisperse sedimenting haze to match the ground-based and spacecraft observations of Titan.⁸ Results for n are in good accord ($n \approx 1.65$ in the near UV, visible, and near IR). Results for k are compared in Figure 4 with Titan tholin, several other tholins, and type II terrestrial kerogen (which is spectrally similar to the organic residue from the Murchison carbonaceous chondrite meteorite). There is a perhaps 30% offset, which may conceivably be dose-related. However, 30% is also the probable error in the laboratory measurement of k , while values extracted from Voyager observations of Titan have an uncertainty²³ of perhaps a factor of 2. Given 3 orders of magnitude variation in k , over a wavelength range from near UV to far IR (but with no Titan data available between 3 and 20 μm), the agreement of Titan tholin with the Titan haze is striking. It explains the reddish coloration very well. Note windows in the near IR (corresponding also to windows in the gas-phase spectrum) which may permit remote imaging of Titan's surface.

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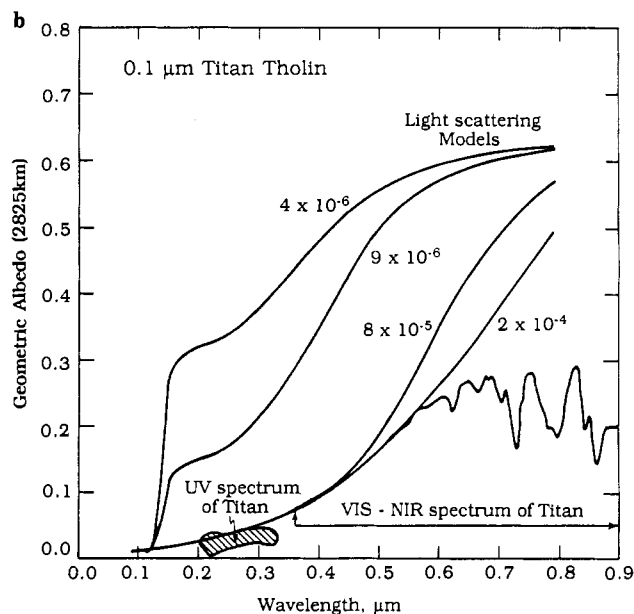
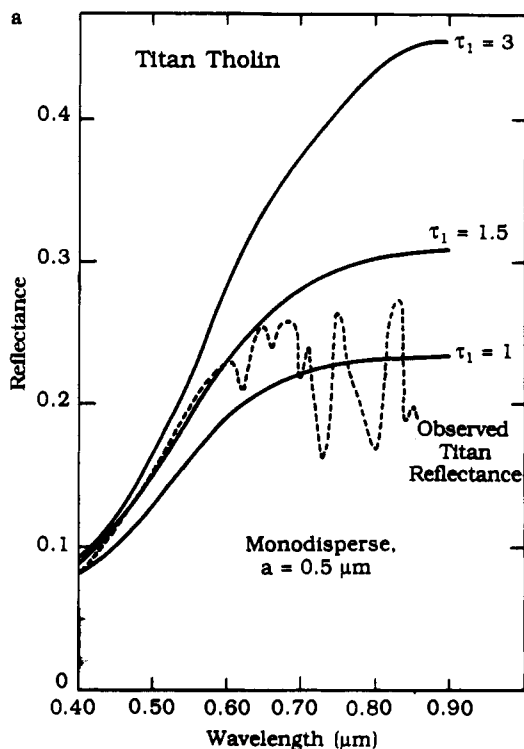


Figure 3. (a) Early (1983) two-stream radiative-transfer spectral calculations of the reflectivity of monodisperse ($r \approx 0.5 \mu\text{m}$) Titan tholin aerosols, compared with observations. (CH₄ absorption ceases at $\lambda \lesssim 550$ nm, so comparisons are readily made in this unobscured wavelength range.) From refs 20 and 21. (b) Early (1984) doubling/adding radiative-transfer calculations for monodisperse ($r \approx 0.1 \mu\text{m}$) Titan tholin aerosols, compared with observations. The shaded area corresponds to IUE data. The curves are labeled with haze column density in grams/square centimeter above a dark surface. CH₄ overtone absorption bands (longward of 550 nm) are not included in the calculation, but between 550 and 350 nm for $2 \times 10^{-4} \text{ g cm}^{-2}$, Titan's reflection spectrum and the model results are indistinguishable within the probable errors. From ref 22. Modern models (e.g., ref 8) are still unable to match visible and near-ultraviolet data perfectly with a single set of model parameters.

From far-IR observations, the mesospheric tholin abundance above the main cloud and haze deck at about 2725 km is estimated²⁴ at several micrograms/

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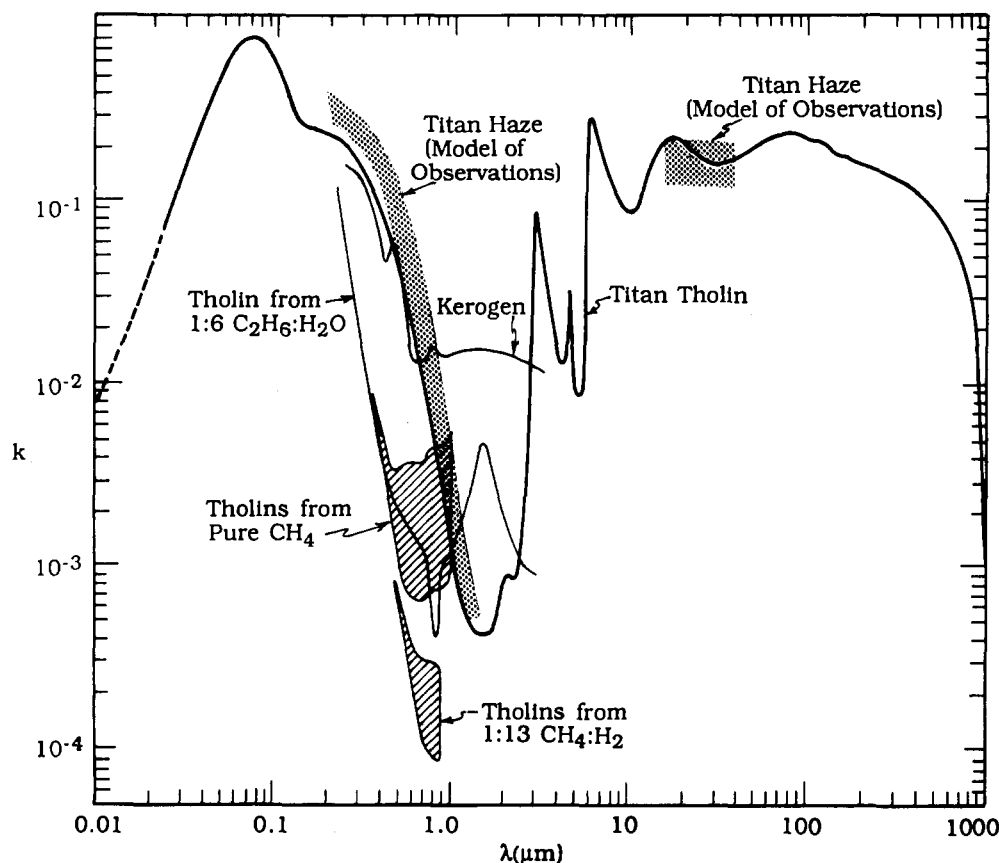


Figure 4. Imaginary part of Titan's complex refractive index (stippled strip at center and top right) deduced from Voyager observations (ref 8) with an assumed dispersion at UV-vis-near-IR wavelengths $\pm 30\%$, compared to type II kerogen (ref 33), Titan tholin generated by irradiating 9:1 N_2/CH_4 (ref 19), and tholins from 13:1 H_2/CH_4 (ref 34), from pure CH_4 (ref 34), and from 6:1 H_2O/C_2H_6 (ref 35). The $\pm 30\%$ probable error is actually associated with the laboratory measurements, but is here attached to the Titan measurements to avoid hopelessly cluttering the figure. Probable errors in our observational knowledge of k for the Titan haze are closer to a factor of 2 (ref 23).

square centimeter (see also ref 8). Comparable values emerge from International Ultraviolet Explorer (IUE) Earth satellite data on the Rayleigh absorbers.²⁵ The sedimentation time to the surface of these submicron aerosols is $3 \times 10^{8 \pm 1}$ s, corresponding to sedimentation fluxes $\sim 10^{-14 \pm 1}$ g cm^{-2} s^{-1} and a sedimentary column of tholins accumulated over the lifetime of Titan of $10^{1 \pm 1}$ m (cf. refs 8, 25, and 26). If there are hydrocarbon oceans on Titan, the tholins will exist chiefly as a submarine deposit, because virtually no organic compounds will float in liquid ethane/methane.²¹

What is the composition of these tholins? CH, C \equiv N, and CC functional groups are evident in $k(\lambda)$ (cf. Figure 4) and expected from the gas-phase products that are presumably²⁷ the tholin precursors. Acid hydrolysis yields a rich array of racemic amino acids, both biological and nonbiological, plus abundant urea (Table I).²⁸ Amino acid yields are $\sim 1\%$ by mass of tholin; their precursors are formed, it is suggested, from chain-addition reactions of the most abundant gas-phase species.²⁷ Two-step laser mass spectrometry reveals $\sim 10^{-4}$ g/g two- to four-ring polycyclic aromatic hydrocarbons (PAHs) in Titan tholin; larger amounts

Table I
Amino Acids and Urea Identified in Acid-Treated Tholin^a

	mg/g ^b
glycine	5.30
alanine	0.70
α -amino- <i>n</i> -butyric acid	0.10
valine	t
threonine	t
aspartic acid	1.10
glutamic acid	0.40
β -alanine	1.20
β -amino- <i>n</i> -butyric acid	0.20
β -aminoisobutyric acid	0.13
γ -amino- <i>n</i> -butyric acid	0.30
α -aminoisobutyric acid	0.06
α -methyl- α -amino- <i>n</i> -butyric acid (isovaline)	t
α,β -diaminopropionic acid	0.10
α,γ -diamino- <i>n</i> -butyric acid	0.02
<i>N</i> -methylglycine	0.18
urea	10.30
amino acids	9.79
urea	10.30

^a After ref 28. ^b Note: t = trace amounts.

of higher PAHs may also be present.²⁹ The volatile component of Titan tholin was examined by sequential and nonsequential pyrolytic GC/MS; over 100 products are detected, including saturated and unsaturated aliphatic hydrocarbons, nitriles, PAHs, amines, pyrroles,

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pyrazines, pyridines, pyrimidines, and the purine, adenine.³⁰ While conceivably some of these products are synthesized in the pyrolysis step, there are reasons for thinking this is not a major effect.^{13,28} The subsequent chemistry of this material, episodically flooded with liquid water, and interacting with presumptive C₂H₆/CH₄/N₂ oceans, might lead to a rich and interesting organic chemistry.

When, in 1973-1974, tholins were first suggested for Titan, "gas chromatograph/mass spectrometer entry probes into the Titanian atmosphere" were urged.¹ Such instruments are currently included in the joint NASA/European Space Agency Cassini/Huygens mission and, some time after the turn of the millennium, might conceivably shed considerable light not just on Titan's organic chemistry but also on the early Earth's.

Future Work

Suggestions for extending the simulation and analytic work described above include

1. better simulations, including lower pressures, temperatures, and CH₄ mass fractions, with control of wall effects;
2. inclusion of 1-100 ppm amounts of CO, detected by recent millimeter wave observations;³⁶

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3. study of the dose and composition dependence of tholin optical constants;
4. simultaneous UV/electron irradiation experiments;
5. analysis of laboratory simulation products, both gases and aerosol solids, by Cassini/Huygens proof test instruments.

Jupiter

Similar work on both gas-phase organic products and tholins is underway for the experimentally more difficult atmosphere of Jupiter, where there is a roughly 1000:1 H₂/He dilution of NH₃/CH₄/H₂O, and in which the cloud structure and optical properties are complex and heterogeneous (e.g., refs 37 and 38). The multi-colored clouds of Jupiter may include tholins as important chromophores, but elemental sulfur, elemental phosphorus, and their compounds have also been suggested.³⁹ The first entry probe into the atmosphere of a Jovian planet is aboard the Galileo spacecraft, scheduled to encounter Jupiter in late 1995. The probe includes a mass spectrometer designed to return in situ data on atmospheric chemistry down almost to the predicted level of the deep aqueous ammonia clouds. While the high-gain antenna of the Galileo spacecraft is at the present writing stuck in an unusable position, all entry probe data can be returned by a low-gain antenna currently working to specifications.

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Energy Flow from Excited Molecules on Salt Surfaces

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Why Study Salt Surfaces?

Sodium chloride was one of the first crystal structures assigned by W. H. Bragg at the birth of X-ray crystallography.¹ The electric fields resulting from the charges of the ions together with a reasonable form for their repulsive interaction can account for the face-centered cubic structure of the crystal as well as for its

binding energy, as reviewed in Pauling's classic book.² Indeed, the ionic solid exhibits such ideal behavior that it is the favored example for introductory discussions of crystallography, phonon behavior, and thermodynamic properties in physical chemistry³ and physics⁴ texts. The surface of salt is also of historical interest. One of the early demonstrations of the wave properties of matter was from observations of helium diffraction

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