Production and Condensation of Organic Gases in the Atmosphere of Titan

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The rates and altitudes for the dissociation of atmospheric constituents of Titan are calculated for solar UV, solar wind protons, interplanetary electrons, Saturn magnetospheric particles, and cosmic rays. The resulting integrated synthesis rates of organic products range from 10^2 - 10^3 g cm⁻² over 4.5 \times 10⁹ years for high-energy particle sources to 1.3 \times 10⁴ g cm⁻² for UV at λ < 1550 Å, and to 5.0×10^5 g cm⁻² if $\lambda > 1550$ Å (acting primarily on C₂H₂, C₂H₄, and C₄H₂) is included. The production rate curves show no localized maxima corresponding to observed altitudes of Titan's hazes and clouds. For simple to moderately complex organic gases in the Titanian atmosphere, condensation occurs below the top of the main cloud deck at 2825 km. Such condensates comprise the principal cloud mass, with molecules of greater complexity condensing at higher altitudes. The scattering optical depths of the condensates of molecules produced in the Titanian mesosphere are as great as $\sim 10^2/(\text{particulate radius}, \mu \text{m})$ if column densities of condensed and gas phases are comparable. Visible condensation hazes of more complex organic compounds may occur at altitudes up to ~3060 km provided only that the abundance of organic products declines with molecular mass no faster than laboratory experiments indicate. Typical organics condensing at 2900 km have molecular masses = 100-150 Da. At current rates of production the integrated depth of precipitated organic liquids, ices, and tholins produced over 4.5×10^9 years ranges from a minimum ~ 100 m to kilometers if UV at $\lambda > 1550$ Å is important. The organic nitrogen content of this layer is expected to be $\sim 10^{-1} - 10^{-3}$ by mass.

INTRODUCTION

It has long been known, since Kuiper's (1944) spectroscopic discovery, that Titan holds a reducing atmosphere composed at least in part of the simplest organic molecule, methane (see also Trafton, 1972). Subsequent photometric and polarimetric observations indicated a very red, ultraviolet-absorbing material (Harris, 1961; see also Caldwell, 1974), probably distributed in and above a thick cloud deck (Veverka, 1973; Zellner, 1973). Knowing that photolysis of CH₄ alone leads to a range of complex hydrocarbons, and that dissociation of CH₄ and other cosmically abundant reduced compounds leads to dark red organic heteropolymers (cf. Khare and Sagan, 1973), it was natural to suggest that the clouds of

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Titan might be composed, at least in part, of complex organic molecules (Sagan, 1971, 1973, 1974; Khare and Sagan, 1973). The quantities of organic molecules synthesized on Titan over geologic time as the result of UV and charged particle synthesis were estimated to be at least hundreds of grams per square centimeter (Sagan, 1974; Hunten, 1977; Chang *et al.*, 1979).

The hypothesis of abundant organic matter in the atmosphere of Titan was supported by the identification of infrared emission features (Gillett *et al.*, 1973; Gillett, 1975) of the hydrocarbons C_2H_2 , C_2H_4 , and C_2H_6 in an atmospheric inversion (Danielson *et al.*, 1973). The Voyager infrared spectrometer (IRIS) experiment (Hanel *et al.*, 1981; Maguire *et al.*, 1981; Kunde *et al.*, 1981) clearly established the presence of aliphatic hydrocarbons up to C_3 , substituted acetylenes, and nitriles. A

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Name	Abundance	Reference
Nitrogen	~85-77%	4,8,9
Argon	$\sim 12 - 17\%$ (?)	4.9
Methane	3-6%	1.4.6.7
Hydrogen	0.1-0.4%	4.6
Ethane	20 ppm	i
Propane	20-5 ppm	2.10
Ethyne (acetylene)	2 ppm	1
Ethene (ethylene)	0.4 ppm	1
Methanenitrile (hydrogen cyanide)	0.2 ppm	1
Butadiyne (diacetylene)	0.03 ppm	3
Propyne (methylacetylene)	0.03 ppm	2
Propynenitrile (cyanoacetylene)	0.1~0.01 ppm	3
Ethanedinitrile (cyanogen)	0.1-0.01 ppm	3
Carbon dioxide	0.01 ppm	5
Carbon monoxide	60 ppm	Ĥ
	Name Nitrogen Argon Methane Hydrogen Ethane Propane Ethyne (acetylene) Ethene (ethylene) Methanenitrile (hydrogen cyanide) Butadiyne (diacetylene) Propyne (methylacetylene) Propynenitrile (cyanoacetylene) Ethanedinitrile (cyanogen) Carbon dioxide Carbon monoxide	NameAbundanceNitrogen~85-77%Argon~12-17% (?)Methane-3-6%Hydrogen0.1-0.4%Ethane20 ppmPropane20-5 ppmEthyne (acetylene)2 ppmEthene (ethylene)0.4 ppmMethanenitrile0.2 ppm(hydrogen cyanide)0.03 ppmButadiyne0.03 ppm(diacetylene)9.03 ppm(cyanoacetylene)0.1-0.01 ppmEthanedinitrile0.1-0.01 ppm(cyanoacetylene)0.1-0.01 ppmCarbon dioxide0.01 ppmCarbon monoxide60 ppm

TABLE I Gaseous Constituents of the Atmosphere of Titan

References and notes: (1) Hanel *et al.*, 1981; (2) Maguire *et al.*, 1981; (3) Kunde *et al.*, 1981; (4) Samuelson *et al.*, 1981; (5) Maguire *et al.*, 1982; (6) Thompson and Sagan, 1984; (7) Smith *et al.*, 1982b; (8) Broadfoot *et al.*, 1981.

(9) Owen (1982) explains why ³⁶Ar hydrate is expected to have condensed during the formation of Titan. The ranges of N_2 and ³⁶Ar abundance are determined by keeping the bulk molecular mass 28.6 Da [see (4)] over the listed range of CH₄ abundance.

(10) The originally published propane abundance of 20 ppm has been reestimated tentatively as 5 ppm (R. E. Samuelson, 1983, personal communication).

(11) Lutz *et al.*, 1983. The detection of CO postdates our computations of UV energy deposition, so CO is not included in this study. Since the electronic spectrum of CO is very similar to that of N_2 [see Okabe (1978)], the effect of CO on our computed energy deposition profiles would be insignificant.

summary of compounds detected or inferred in Titan's atmosphere is given in Table I. All observed gas phase organics have been produced in laboratory experiments by sparking, electron-irradiating, or ultraviolet-irradiating a mixture of N₂ and CH₄ in approximately the Titan atmospheric proportions (Balestic, 1974; Toupance *et al.*, 1975; Scattergood *et al.*, 1975; Scattergood and Owen, 1977; Gupta *et al.*, 1981; Raulin *et al.*, 1982).

Ultraviolet, infrared, optical imaging, and radio occultation experiments conducted during the Voyager 1 and 2 encounters with Titan, in November 1980 and August 1981, revealed a deep N_2/CH_4 atmosphere overlying a surface at 2575 km and temperature 94°K (Hanel *et al.*, 1981; Tyler *et al.*, 1981; Broadfoot *et al.*, 1981), with a thick, opaque, and nearly featureless cloud deck extending up to about 2825 km, and distinct limb hazes above the main cloud deck at altitudes ranging to about 2930 km (Smith *et al.*, 1982a; Rages and Pollack, 1983). Haze layers merge with the main cloud deck toward Titan's north pole; separation increases toward the south and multiple haze layers are apparently present at high southern latitudes (Smith *et al.*, 1981, 1982a).

The pressure-temperature profile for Titan's atmosphere, derived from Voyager radio occultation and IRIS experiments (Hanel et al., 1981; Tyler et al., 1981; Samuelson et al., 1981), together with the compositional information summarized in Table I, defines the first basic reference atmosphere for Titan. In addition, Voyager 1 and 2 measurements provide important new information on the energy spectrum of energetic protons and electrons in Saturn's magnetosphere (Krimigis et al., 1981, 1982; Vogt et al., 1981, 1982). We use this information to investigate the altitude-dependent energy deposition and dissociation rates from solar ultraviolet radiation, energetic protons and electrons from Saturn's magnetosphere, cosmic rays, solar wind protons, and interplanetary (solar wind and cosmic ray) electrons.

ENERGY SOURCES

For both UV and charged particles, the propagation, deposition, and averaging of energy input over Titan's extended atmosphere are done as follows: In all computations the unit pathlength ds is taken to be 0.1 km. Energy deposition is computed for a number of paths, each characterized by an impact radius R_{\min} , from the center of Titan's disk up to a maximum impact radius of 3900 km. For paths intersecting the solid disk of Titan ($R_{min} < 2575$ km), integration terminates at the surface, while for supralimb paths it continues upward through the atmosphere after passing $R = R_{\min}$. Integrations are started at 4000-km radius. When the radius R from planet center crosses a boundary value [defined as a change of 0.1 in log p, or about 16 km at R = 3500 km], the accumulated energy deposition per cubic centimeter is computed, resulting in an effective altitude resolution of 10-20 km. For solar UV and solar wind protons and electrons, the intercepting area of Titan's atmosphere is taken as its planar projection. For Saturn high energy particles, the intercept area is twice this value, while the full area of Titan receives the cosmic ray

flux. For each energy source, the rate of energy deposition per unit area at Titan's surface (R = 2575 km) is then calculated by an area-weighted integration over altitude.

Solar Ultraviolet Radiation

 N_2 is ionized, dissociated, or predissociated by $\lambda < 1000$ Å, and Ar is ionized by $\lambda < 780$ Å, while the CH₄ absorption continuum is significant at $\lambda \leq 1550$ Å. From photochemical models (Strobel, 1974; Allen *et al.*, 1980), we adopt an efficiency, for these high energy photochemical processes to incorporate CH₄ into organic products, of unity. In practice this means that we require ~10 eV (about 1 photon) per heavy atom incorporated for photochemical processes initiated by N₂, Ar, and CH₄ absorption.

Wavelengths $\lambda > 1550$ Å provide an additional energy source which is utilized with varying efficiency by the organic compounds which have been detected in Titan's atmosphere (Table I), and undoubtedly by many undetected species as well. We call this energy source "secondary UV," because it represents the energy deposited by solar UV into organic molecules which are themselves the products of synthetic processes in Titan's atmosphere. For simplicity, we assume for this longer wavelength UV the same net efficiency for the conversion of energy into synthetic products as for charged particles (see next section), about 32 eV per heavy atom incorporated. This translates to a quantum yield varying from about 0.25 for 1550-Å photons to 0.15 for 2600-Å photons. While more complex than methane, the organic compounds listed in Table I are sufficiently simple that electronic excitation generally results in dissociation or predissociation with a quantum yield of this order (see, e.g., Okabe, 1978). A high yield for C incorporation by secondary UV has been demonstrated for C₂H₂ and higher acetylenes (oligoacetylenes) by Allen et al. (1980). For molecules more complex than those considered here (especially aromatic ring systems), electronic excitation does not generally lead to dissociation, and such quantum yields will be $\ll 0.1$.

The UV absorption spectra for compounds included in this study are compiled from the sources listed in Appendix I. For all compounds, a constant abundance equal to that listed in Table I is assumed. This assumption is consistent with the nature of the IRIS measurements, which give a mean column abundance above an assumed condensation level (Hanel et al., 1981; R. E. Samuelson, 1983, personal communication). While we realize that the synthetic processes will naturally lead to nonuniform abundance profiles for each compound (see, e.g., Yung et al., 1984), a full treatment of Titanian atmospheric photochemistry is not intended: such a treatment is in any case preliminary (although instructive), even for simple organics, since the rates of many important reactions must be estimated (Strobel, 1982).

Compiled spectra are smoothed to 50-Å resolution, and over each 50-Å interval from 50 to 2600 Å the energy deposited along a given path through the atmosphere is computed from

$$a_{\nu} = \sum_{i} X_{i} a_{\nu,i}; \qquad dF_{\nu} = -a_{\nu} \rho F_{\nu} ds;$$
$$dE_{i} = X_{i} \sum_{\nu} (a_{\nu,i}/a_{\nu}) dF_{\nu}$$

where $a_{\nu,i}$ is the absorption coefficient [(cmam)⁻¹] of the *i*th constituent over a frequency interval with midpoint ν ; a_{ν} is the total atmospheric absorption coefficient; X_i is the mole fraction of the *i*th constituent; F_{ν} is the flux of radiation (erg cm⁻² sec⁻¹) in the interval; ρ is the local atmospheric density in amagats (where 1 amagat = $2.686 \times$ 10^{19} molec. cm⁻³ = 0.04462 mole liter⁻¹); dF_{ν} is the incremental change in intensity in the interval; ds is the pathlength increment; and dE_i is the incremental energy deposition (erg cm⁻² sec⁻¹) into species *i*. The solar UV flux (F_{ν}) at $\lambda < 2000$ Å is taken from Heroux and Hinteregger (1978) and at $\lambda >$ 2000 Å from Arvesen et al. (1969).

Saturn Magnetospheric High Energy Particles

Saturn magnetospheric proton and electron fluxes were measured by Voyagers 1 and 2 (Krimigis et al., 1981, 1982; Vogt et al., 1981, 1982). The observed counting rates, when divided by appropriate geometric factors (Krimigis et al., 1977; Stone et al., 1977), yield particle fluxes over an energy range ΔE , which we call differential fluxes, $N(E,E + \Delta E) = N_D(E)$, or fluxes for all energies greater than a cutoff $E_{\rm C}$, which we call integral fluxes, $N(E > E_{\rm C}) = N_{\rm I}(E)$. In the limit of small ΔE , $N/\Delta E$ becomes a true differential flux which we measure in particles cm⁻² sec⁻¹ sr⁻¹ MeV⁻¹. For a power-law distribution in energy $N_{\rm D}(E) =$ $N_0(E/E_0)^{\zeta}$ the integral flux

$$N_{I}(E) = \int_{E}^{\infty} N_{0}(E'/E_{0})^{\zeta} dE'$$

= - [E/(\zeta + 1)]N_{D}(E), (\zeta < -1).

Thus $N_{\rm D}(E) = N/\Delta E$ for small ΔE ; or $N_{\rm D}(E) = -(\zeta + 1)N_{\rm I}(E)/E$ for integral fluxes. Published counting rates are converted to differential fluxes by one of these two relations, as appropriate. The results for Saturn magnetospheric electrons are shown in Table II and Fig. 1. A single power law fits the differential fluxes at Titan's Saturnicentric distance at both spacecraft entry [near 20° phase angle for both Voyagers] and exit [near 130° phase angle for Voyager 1 and near 105° for Voyager 2 (Ness *et al.*, 1982)]. The electron flux does not vary significantly with longitude. The flux is well-represented by

$$\log(N_{\rm e}) = 1.43 - 3.10 \log(E_{\rm MeV}), -1.43 < \log(E_{\rm MeV}) < 0.41.$$

In contrast, the Saturn magnetospheric proton flux (Table III and Fig. 2) shows a strong dependence on phase angle. Fluxes at spacecraft entry and spacecraft exit fall on separate lines in log-log plots, with the proton flux at spacecraft entry given by

$$log(N_{\rm p}) = 0.93 - 3.35 \, log(E_{\rm MeV}), -1.55 < log(E_{\rm MeV}) < 0.26,$$

TABLE II



FIG. 1. Differential energy spectrum of Saturn magnetospheric electrons from Voyager LECP and CRS experiments. \triangle , Voyager 1, inbound; ∇ , Voyager 1, outbound; λ , Voyager 2, inbound; Υ , Voyager 2, outbound. The magnetospheric electron differential energy spectrum is well-represented by a single power law with exponent $\zeta = -3.1$.



FIG. 2. Differential energy spectrum of Saturn magnetospheric protons from Voyager LECP and CRS experiments. \triangle , Voyager 1, inbound; ∇ , Voyager 1, outbound; A, Voyager 2, inbound; Y, Voyager 2, outbound. Magnetospheric proton flux decreases substantially away from the subsolar longitude. Differential energy spectra inbound and outbound are characterized by $\zeta = -3.4$ (upper line) and -3.0 (lower line), respectively.

		A REAL PROPERTY AND A REAL PROPERTY A REAL PROPERTY AND A REAL PROPERTY A REAL PRO						
Expt ^a	Energy range (MeV)	Count rate.in (sec ⁻¹)	Count rate.out (sec ⁻¹)	Geom. factor (cm ² sr)	Intensity.in (cm ⁻² sec ⁻¹ sr ⁻¹)	Intensity, out ($cm^{-2} \sec^{-1} sr^{-1}$)	$N_{\rm D}(E)$,in (cm ⁻² sec ⁻¹ sr ⁻¹ MeV ⁻¹)	$N_{\rm D}(E)$,out (cm ⁻² sec ⁻¹ sr ⁻¹ MeV ⁻¹)
LECP	0.022-0.035	001	15	0.002	5. × 10 ⁴	8. × 10 ³	5. × 10°	7. × 10 ⁵
LECP	0.037-0.070	04	50	0.002	2. $\times 10^4$	2.5×10^4	1.1×10^{6}	1.4×10^{6}
CRS	0.14 - 0.4	200	1500		2. $\times 10^2$	1.5×10^{3}	$3. \times 10^{3}$	$2. \times 10^4$
CRS	0.15 - 0.4	2000	4000	-i	2. $\times 10^{3}$	4. $\times 10^{3}$	$3. \times 10^{4}$	6. $\times 10^{4}$
LECP	0.2 - 0.5	0.4	0.7	0.002	$2. \times 10^{2}$	4. $\times 10^{2}$	2. $\times 10^{3}$	4. $\times 10^{3}$
LECP	0.25-2.0	-	-	0.002	$5. \times 10^{2}$	$5. \times 10^{2}$	4. $\times 10^{3}$	4. $\times 10^{3}$
CRS	>0.35	001	150	1.3	$8. \times 10^{1}$	1.1×10^{2}	5. $\times 10^{2}$	7. $\times 10^{2}$
CRS	>0.60	20	20	~	1.0×10^{1}	1.0×10^{1}	$4. \times 10^{1}$	4. × 10 ¹
CRS	>0.60	20	20	ri	1.0×10^{1}	1.0×10^{1}	4. $\times 10^{1}$	4. \times 10 ¹
CRS	>2.5	3	3	1.	3.	3.	2.5	2.5
CRS	>2.6	~	~		з.	3.	2.5	2.5

^a LECP, Krimigis et al., 1981, 1982; CRS, Vogt et al., 1981, 1982.

rafi	Expt"	Energy range (MeV)	Count rate.in (sec ¹)	Count rate out (sec ⁻¹)	Geom. factor (cm ² sr)	Intensity,in (cm ⁻² scc ⁻¹ sr ⁻¹)	Intensity out (cm $\frac{2}{5}$ sec $^{-1}$ sr $^{-1}$)	$\frac{N_{\rm D}(E).in}{(\rm cm^{-2} sec^{-1})}$	$N_{\rm D}(E)$, out fcm $\frac{2}{2} \sec^{-1}$ sr $^{-1}$ MeV $^{-1}$
2	LECP	0.028-0.043	009	30	0.12	$5. \times 10^{3}$	1.7 × 10 ²	4, × 10 ⁵	1.2 × 10 ⁴
12	LECP	0.053 - 0.085	200	30	0.12	1.7×10^{3}	2 102	8. $\times 10^{4}$	8. $\times 10^{3}$
22	LECP	0.080-0.137	(009	7	0.12	$5. \times 10^3$	$6. \times 10^{1}$	1.5×10^{5}	1.5×10^3
Š	LECP	0.22 - 0.54	100	0.3	0.12	$8. \times 10^2$	ci	$8. \times 10^3$	1.8×10^{1}
17	CRS	>0.43	0£	08	0.44	$7. ~ 10^{5}$	7. × 10 ¹	4. $\times 10^{2}$	$3. \times 10^{2}$
2	CRS	>0.43	100	7	0.44	$2 \sim 10^2$	1.6×10^{1}	1.2×10^{3}	$7. \times 10^{1}$
17	LECP	0.55 -1.05	0.2	0.1	0.12	ci	8. × 10 ⁻¹	×	, e
Ś	LECP	0.99 -2.10	0.2	0.04	0.12	ci	1. J. 10 1	×.	6. × 10 ⁻¹
17	CRS	1.8 -8	I		I	2.5×10^{-1}	1.5×10^{-1}	3. + 10 ⁻¹	1.6 - 10

and that measured at spacecraft exit by

$$\log(N_{\rm p}) = -0.21 - 3.02 \log(E_{\rm MeV}), \\ -1.55 < \log(E_{\rm MeV}) < 0.26.$$

Since particle flux at high Saturn phase angles $(>100^\circ)$ is reduced more than tenfold, the energy contributed to Titan's atmosphere in that part of each orbit near Saturn's subsolar longitude is dominant. We employ the power law applicable for spacecraft entry, and divide the computed energy deposition due to magnetospheric protons by 4 as an estimate of the fraction of time Titan spends in the high flux part of its orbit.

Energy deposition rates for high energy electrons are computed from (Moyer, 1958)

$$dE = -\frac{2\pi e^4 n_e}{m_e v^2} \left[\ln \left(\frac{m_e c^2}{I} \right)^2 + \ln \frac{\beta^2 \gamma^4}{4} \left(\frac{\gamma - 1}{2\gamma - 1} \right) + \frac{1}{\gamma^2} \right] ds$$

where e = electron charge, $m_e =$ electron mass, $n_{\rm e}$ = mean electron density of the medium (cm⁻³), v = particle speed, c = speed of light, I = average ionization potential for the medium, $\beta \equiv v/c$, and $\gamma \equiv E_{\text{Total}}/c$ $m_{\rm e}c^2$. For nuclear particles, energy loss is computed (Moyer, 1958) using

$$dE = -\frac{4\pi Z_{\rm N}^2 e^4 n_{\rm e}}{m_{\rm e} v^2} \left[\ln \left(\frac{2m_{\rm e} v^2}{1} \right) + \ln(1 - \beta^2) - \beta^2 \right] ds$$

where Z_N is the nuclear charge. The value of I is estimated as $I \simeq 13.5 Z_N$ (eV) (Moyer, 1958). The differential energy loss is integrated through the various atmospheric paths to determine energy deposition as a function of altitude.

Energetic Particles from the Interplanetary Medium

⁴ I.ECP, Krimigis et al., 1981, 1982; CRS, Vogt et al., 1981, 1982

Although Titan's orbit is usually contained completely within Saturn's magnetosphere, this was not the case at the Pioneer 11 encounter (van Allen et al., 1980). The solar wind at Saturn has a density of about

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TABLE III

0.2 cm⁻³, velocity ~500 km sec⁻¹, and random-kinetic temperature of about $10^{4.8}$ °K (Wolfe *et al.*, 1980). Mean proton thermal velocity is ~40 km sec⁻¹, so advective energy dominates. The quiet-time solar wind provides protons of about 1.3 keV energy at a rate ~1 × 10^7 cm⁻² sec⁻¹. Titan's orbit is estimated to lie partly beyond the magnetopause about one-fifth of the time (H. S. Bridge, 1981, personal communication). Since it is unlikely that more than one fourth of Titan's orbit is exposed during those periods, we reduce computed solar wind energy input by a factor of 20.

Cosmic ray energy deposition at Titan has been discussed by Capone *et al.* (1981, 1983). The flux of cosmic ray protons and He nuclei with $E > 10^3$ MeV is taken from Juliusson (1975), while lower energy cosmic ray fluxes measured near minimum solar activity are taken from Meyer (1969). Propagation and energy deposition are computed as explained for Saturn magnetospheric particles.

Electrons in the interplanetary medium have an energy spectrum which varies smoothly from the "thermal core" solar wind electrons of $T \approx 3.5 \times 10^5$ °K through higher energy solar-derived electrons to secondary and primary cosmic ray electrons. The differential intensity spectrum for electrons from thermal energies to 10⁶ MeV is taken from the summary of Lin *et al.* (1972). Since the Saturnian magnetosphere shields Titan from the solar wind electrons most of the time, energy deposition above 3450 km is reduced by a factor of 20.

RATES AND ALTITUDES OF ORGANIC SYNTHESIS

Energy Deposition Rates

The globally averaged power dissipated per unit volume, Γ , for these energy sources is shown in Fig. 3. Above 3300 km, the deposition of solar UV energy into the primary atmospheric constituents N₂ and CH₄ dominates, while Saturn magnetospheric electrons deposit energy at a similar rate between 3300 and 3050 km. We conclude that molecules synthesized by solar UV and Saturn magnetospheric electrons are likely to be responsible for the EUV opacity seen by Voyager 1 between 3200 and 3600 km (Smith *et al.*, 1982b). Saturn magnetospheric protons are a significant energy source above 3100 km, but are less important than magnetospheric electrons.

Solar wind electrons deposit energy primarily above 3450 km, and while their average power dissipation (Fig. 3) is small compared to that of solar UV, the energy input rate when Titan is actually exposed to the solar wind is a factor of 20 higher and can temporarily exceed that of solar UV. (Thus, secular changes in production rates of high altitude chromophores may conceivably be detectable as Titan moves across the Saturnian magnetopause through the solar cycle.) Solar wind protons deposit their energy above 3900 km. Since energetic events at high altitudes lead primarily to atmospheric escape and not to synthesis (Strobel and Shemansky, 1982; Capone et al., 1983), energy deposition by low energy charged particles above 3900 km is not counted as energy available for organic synthesis.

The UV energy input to N_2 and CH_4 is less significant than other sources below 3300 km, but the absorption of longer wavelength UV by more complex molecules in Titan's atmosphere increases rapidly below 3200 km and becomes by far the most significant energy source in Titan's lower atmosphere. In Fig. 3 the solid curve (with broad dashes below 2900 km) is the total power from all sources, while the curve with short dashes is the total power from all sources other than secondary UV. While absorption by atmospheric gases only (as shown in Fig. 3) would lead to the dominance of secondary UV throughout the lower atmosphere, in reality scattering will cause most of these photons to be deposited within an aerosol scale height of the top of the main cloud deck, near 2825 km. Cos-



FIG. 3. Variation of disk-integrated, globally averaged energy deposition rate (Γ) with altitude for UV and charged particle energy sources in Titan's atmosphere. Each curve is labeled with the energy source whose deposition rate through the atmosphere it defines. Every energy source shown is sufficient to produce >10 g cm⁻² of accumulated organic products over geological time. Solar UV absorbed by major atmospheric constituents (primarily $\lambda < 1500$ Å and above 3200 km), Saturn magnetospheric electrons, and UV absorbed by minor constituents (primarily $\lambda > 1500$ Å and below 3200 km) are ordinarily the dominant energy sources in Titan's atmosphere. When Titan lies outside the Saturnian magnetopause, the solar wind electron flux can be a factor 20 larger than shown here. The "Total" line is dashed below 2900 km to indicate that long-wavelength solar UV, because of scattering and particulate absorption, will actually be deposited mainly near the top of the main cloud deck, instead of deep in the lower atmosphere as indicated here.

mic ray nuclei and electrons are significant energy sources near Titan's surface, and may be more important than secondary UV if, as seems likely, the optical depth of the overlying cloud is large.

Synthesis and Surface Accumulation

The integrated energy input above 3000 km corresponds to a synthesis rate of 1×10^{-13} g cm⁻² sec⁻¹, or about 3 μ g cm⁻² ($\sim 3 \times 10^{-2} \mu$ m) per year, while the rate in Titan's clouds and lower atmosphere, due almost exclusively to long-wavelength UV, exceeds this by a factor of 40. In Table IV we present, for each energy source, the vertically integrated dissociation and synthesis rates normalized to unit area at Titan's surface. Every one of the energy sources considered can produce at least 100 g cm⁻² of organic products over 4.5 × 10⁹

years (4.5 AE). Primary UV energy, initiating synthesis through dissociation of CH_4 and N_2 , can result in the deposition of 12 kg cm⁻² of organic products at Titan's surface, while secondary UV, if utilized as efficiently as assumed, could produce hundreds of kilograms per square centimeter of products.

These accumulated organics are expected to be a mixture of relatively simple products such as those detected by IRIS, complex organic heteropolymers (tholins) which are produced by various energy sources in Titan simulation experiments, and, in varying abundances, the entire spectrum of organic compounds of molecular masses intermediate between these extremes. Titan tholin reproduces well the observed spectral properties, particle size, and complex refractive index of the haze

Energy source	Energy flux (erg cm ⁻² sec ⁻¹)	Synthesis rate $[(C + N) \text{ cm}^{-2} \text{ sec}^{-1}]$	Column density (g cm ⁻² over 4.5 AE)
UV, secondary $(\lambda > 1550 \text{ Å})$	$9.0 \times 10^{\circ}$	1.8 × 10 ¹¹	5.0×10^{5}
UV, primary ($\lambda < 1550 \text{ Å}$)	7.3×10^{-2}	4.6×10^{9}	1.3 × 10 ⁴
CH₄	5.0×10^{-2}	3.1×10^{9}	8.9×10^{3}
N ₂	2.1×10^{-2}	1.3×10^{9}	3.7×10^{3}
Ar	1.8×10^{-3}	1.1×10^{8}	3.1×10^{2}
Saturn magnetosphere, energetic electrons	2.4×10^{-2}	4.7×10^{8}	1.3×10^{3}
Cosmic rays	9.0×10^{-3}	1.8×10^{8}	5.0×10^{2}
Interplanetary electrons	3.2×10^{-3}	6.3×10^{7}	1.8×10^2
Saturn magnetosphere, energetic protons	2.2×10^{-3}	4.4×10^{7}	1.3×10^{2}
Energy deposited above 3900 km:			
Solar wind protons	4.8×10^{-2}	9.4×10^{8}	2.7×10^{3}
Saturn magnetospheric plasma	1.9×10^{-2}	3.8×10^8	1.1×10^{3}
Low-Energy interplanetary electrons	1.4×10^{-2}	2.7×10^{8}	7.6×10^2

TABLE IV

NET DISSOCIATION AND SYNTHESIS RATES

and upper cloud of Titan (Sagan and Khare, 1981, 1982; Khare et al., 1982; Sagan et al., 1983). Scanning electron microscopy of tholins (Sagan and Khare, 1981) shows no significant void volume. Since ~90% of common organic compounds composed of C, H, N, and O have densities $\sim 0.7-1.3$ g cm⁻³ (see Sagan and Thompson, 1984), the column density given in Table IV is also the approximate thickness of accumulated surface deposits in centimeters (provided such deposits have not been overpaved or subducted by ongoing geologic activity). Accumulations ranging from hundreds of centimeters for interplanetary high energy charged particles to hundreds of meters for primary UV to several kilometers for secondary UV are indicated. Our most conservative estimate of the thickness of organic precipitate on Titan is ~ 100 meters-assuming no contribution whatever from long wavelength UV, which is clearly unrealistic.

Our total primary UV synthesis rate of 4.2×10^9 (C) cm⁻² sec⁻¹ is very similar to the photolysis rate of CH₄ of 5×10^9 cm⁻² sec^{-1} for periods of quiescent solar activity given by Allen et al. (1980). When photochemical catalysis of CH₄ dissociation by C₂H₂ and oligoacetylenes is included, they compute a total CH₄ incorporation rate of 1 \times 10¹¹ cm⁻² sec⁻¹, based on a primary CH₄ photolysis rate of 1×10^{10} cm⁻² sec⁻¹ for moderate solar activity. This is similar to our secondary UV figure of 1.8×10^{11} (C) $cm^{-2} sec^{-1}$. Although these two approaches are quite different, it is not surprising that our numbers are similar given the dominance of C₂H₂ and C₄H₂ in utilizing longwavelength UV in both studies (see text below and Fig. 4). Also, while based on CH₄ + NH₃ photolysis studies which do not bear directly on Titanian photochemical processes, the synthesis rate due to long-wavelength UV of 1×10^{11} (C + N) cm⁻² sec⁻¹ estimated by Chang et al. (1979) is very



FIG. 4. Energy deposited into major molecular absorbers of solar UV in Titan's atmosphere. Curves are labeled with the chemical formulas, and dashed with a chemical shorthand showing the bond structure of each compound. Open symbol ends [as in C_2H_2 (\equiv)] indicate the presence of H atoms, while closed symbol ends [as in N_2 (\equiv)] indicate a heavy atom terminus. Symbols and net flux absorbed (erg cm⁻² sec⁻¹) for each species are: \exists , N_2 , 2.1×10^{-2} ; \bigcirc , CH₄, 5.0×10^{-2} ; \bigcirc , Ar, 1.8×10^{-3} ; =, C_2H_4 , 4.6×10^{-2} ; \equiv , C_2H_2 , 4.7×10^{-1} ; $\equiv \equiv$, C_4H_2 , 8.5. Absorption below 2825 km will be progressively altered by scattering in the clouds.

similar to the above figures. Our integrated column density of 12 kg cm⁻² over 4.5 AE compares to 30 kg cm⁻² estimated by Hunten (1977) on the basis of a net synthesis rate of C₂H₂ and C₂H₆ of 8×10^9 (C) cm⁻² sec⁻¹ obtained by Strobel (1974).

The product yield over 4.5 AE from Saturn magnetospheric electrons and protons is 1.3 kg cm⁻². This value, based on actual measurements of particle fluxes at Titan's orbital radius by Voyagers 1 and 2, is about three times the value estimated by Chang et al. (1979), which was based on a pre-spacecraft-exploration model of the Saturnian magnetosphere. Our cosmic ray energy deposition profiles are very similar to the production rate profiles of Capone et al. (1981, 1983). Our yield from cosmic rays of 500 g cm⁻² compares to an estimated yield of 185 g cm⁻² quoted in Chang et al. (1979) on the basis of the early work of Capone and collaborators.

The yield from interplanetary electrons is 180 g cm⁻², and is comparable to the 130 g cm⁻² we compute for Saturn magnetospheric protons. This synthesis is distributed over a large range of altitudes, with peak rates at 3500 and 2640 km corresponding to maxima in the energy input from solar wind and cosmic ray electrons, respectively. The higher altitude component is very variable, depending on the extent of Saturn's magnetosphere, while the primary cosmic ray electrons provide a small addition, at similar altitudes, to the energy deposited near the surface by cosmic ray nuclei.

At the bottom of Table IV are given the energy fluxes and equivalent rates of chemical processing for low-energy charged particle sources which deposit their energy above 3900 km. While we have not modeled atmospheric escape in this study, we expect that power input at high altitudes is



FIG. 5. Energy deposited into minor molecular absorbers of solar UV in Titan's atmosphere. Curves are labeled with the chemical formulas, and dashed with a chemical bond shorthand symbol in each case. Symbols and net flux absorbed (erg cm⁻² sec⁻¹) for each species are: —, H₂ 7.6 × 10⁻⁶; –, C₂H₆ 4.9×10^{-4} ; ––, C₃H₈ 1.3×10^{-3} ; **a**, HCN 8.3×10^{-7} ; **b**–**a**, C₂N₂ 1.7×10^{-4} ; **b**–**a**, HC₃N 1.5×10^{-4} ; =–, C₃H₄ 1.6×10^{-4} ; **a**–**a**, CO₂ 5.5×10^{-6} . Absorption below 2825 km will be progressively altered by scattering in the clouds.

reasonably efficient in ejecting C and N atoms (see Strobel and Shemansky, 1982), and these column densities may therefore be thought of as simple estimates of the net loss of C and N over Titan's history. Strobel and Shemansky's computed power dissipation of 2×10^9 W, based on Voyager EUV emission line observations, is equivalent to 2.4×10^{-2} erg cm⁻² sec⁻¹ at Titan's surface. While they assume the energy source to be Saturn low-energy magnetospheric electrons, we note that solar wind protons and electrons appear to input energy at about this rate and are probably also important in exospheric excitation and escape processes.

Lower Atmosphere UV Absorption

In Figs. 4 and 5 are shown the power input by solar UV to each of the molecules in Table I. Figure 4 presents those most active in absorbing solar UV— N_2 , CH₄, and Ar at higher altitudes, and C₂H₄, C₂H₂,

and C₄H₂ at lower altitudes. In the caption to Fig. 4 are the integrated energy fluxes for each of these species. C₄H₂ is by far the most important sink for long-wavelength UV, accounting for 94% of the energy input at low altitudes, while C_2H_2 contributes about 5% of the total, C₂H₄ about 0.5%, and minor components (Fig. 5) the remainder. Because the main cloud deck extends to >2800 km, it is likely that condensed materials, through absorption and scattering, move the absorption of UV to higher altitudes than indicated by this simple model. Also, anticipating the next section, the optical depth of known condensables in the lower cloud (between 2660 and 2620 km) is probably large. While the shapes of the energy deposition/altitude curves in the lower atmosphere are certainly modified by scattering processes, the relative energy deposited in each species should remain about the same. One possible effect of the absorption of UV by condensed materials instead

of by gases is a channeling of more of the energy into the processing of existing organics to higher molecular masses, and less into new synthesis.

If nonsynthetic absorption of UV by tholins in haze and cloud material dominates molecular long-wavelength absorption, the synthesis rate due to secondary UV may be reduced to values substantially below those we and Allen et al. (1980) compute. A satisfactory answer to the question of the fate of long-wavelength UV can eventually be provided by radiative transfer calculations which compute molecular and particulate absorption and scattering to deeper levels in Titan's atmosphere than have been considered to date. Also, the efficiency of longwavelength UV absorption by condensates and tholins, in catalyzing the incorporation of CH₄ into new or more complex organic products, should be investigated experimentally.

In Fig. 5 we show the UV power input to the remaining molecules from Table I. These molecules are much less important than C_4H_2 , C_2H_2 , and C_2H_4 in utilizing solar UV, primarily because their UV spectra extend only to slightly longer wavelengths than that of CH₄. C_3H_8 , the most important power sink in this group, absorbs only 10^{-4} of the total secondary UV input. However, even this seemingly small amount of energy is within an order of magnitude of that input by energetic charged particles (Table IV), and can result in >10 g cm⁻² of products over 4.5 AE.

The likelihood that tholin densities are $\sim 1 \text{ g cm}^{-3}$ implies, for the Toon *et al.* (1980) model of coagulation and sedimentation in the Titanian clouds, an organic production rate $\approx 3.5 \times 10^{-13} \text{ g cm}^{-2} \text{ sec}^{-1}$, corresponding to a column of tholins $\sim 0.5 \text{ km}$ thick deposited over 4.5 AE. This in turn implies (cf. Table IV) that wavelengths longer than the onset of the CH₄ photodissociation continuum near 1550 Å are being utilized for photochemistry on Titan. As the present study and Allen *et al.* (1980) predict, a substantial amount of UV photochemistry via such molecules as C₂H₂, C₄H₂, and C₂H₄

must therefore be taking place—although it follows that the effective synthesis efficiency may be <0.1 of our estimate. This lower conversion efficiency for long-wavelength UV is probably due to multiple scattering and tholin extinction of UV, as mentioned above.

Nitrogenous Organics

Since it appears that solar UV acting on CH₄/N₂ atmospheres produces hydrocarbons almost exclusively, while synthesis induced by high energy particles is efficient in incorporating N into the product molecules (Chang et al., 1979; Raulin et al., 1982), we expect hydrocarbon products to dominate nitriles and other nitrogen-containing organics by at least 6:1, the ratio of UV primary synthesis to high energy particle synthesis in Table IV. In Titan's mesosphere, a lower ratio is found, with HCN and two organic nitriles present at 0.2 ppm or less, while C_2H_6 and C_3H_8 are present at abundances close to 20 ppm (Table I). We expect a similar situation to hold for the total organic precipitate, the bulk of which should be hydrocarbon products (with C_2H_6 and C₃H₈ as major components), and with a nitrogenous component not greater than 1-10% of the total mass. The lighter hydrocarbon products, along with CH_4 and N_2 , probably form a surface ocean (Sagan and Dermott, 1982; Lunine et al., 1983) with a complement of more complex dissolved organics and sediment (see also Thompson and Sagan, 1984). If secondary UV is as important as indicated, the nitrile fraction could be at most $\sim 10^{-3}$ (N atoms per C atom) in the total product at Titan's surface.

It appears that plausible hydrocarbon polymers are not sufficiently absorbing to match the reflectance and polarization properties of Titan's haze. Podolak's (1984) polarization/light-scattering/sedimentation study requires Titan haze particles of imaginary refractive index (n_i) identical to that of Titan tholin (Khare *et al.*, 1984). (Titan tholin is the nitrogenous product of energetic electron bombardment of an N₂/CH₄ atmosphere at pressures relevant to Titan.) Podolak requires a production rate of this strongly absorbing, red material of $3.5 \times 10^{-15} \text{ g cm}^{-2} \sec^{-1} = 2 \times 10^8 (\text{C} + \text{N}) \text{ cm}^{-2} \sec^{-1}$. Saturn magnetospheric electrons can produce $5 \times 10^8 (\text{C} + \text{N}) \text{ cm}^{-2} \sec^{-1}$ of this material high in Titan's mesosphere (Table IV, Fig. 3). Podolak also deduces a production rate of $3.5 \times 10^{-14} \text{ g cm}^{-2} \sec^{-1} = 2 \times 10^9 (\text{C} + \text{N}) \text{ cm}^{-2} \sec^{-1}$ of less absorbing (more conservatively scattering) material. This quantity is easily provided by high altitude, primary UV production for which we compute a rate of $5 \times 10^9 (\text{C} + \text{N}) \text{ cm}^{-2} \sec^{-1}$.

CLOUD AND HAZE CONDENSATION PROCESSES

Altitudes near and above the upper reaches of the main cloud deck correspond to a deep minimum in the net energy deposition rate for energy sources other than secondary UV. Even if the full complement of secondary UV is included, the thin detached limb haze(s) do not seem attributable to some sharp local peak in synthesis rate. Since neither the energy deposition profiles shown here nor photochemical models (Allen *et al.*, 1980; Yung *et al.*, 1984) predict regions of strongly enhanced synthesis near the altitudes of limb hazes, they must form either by condensation of sufficiently abundant organic products diffusing from regions of high production rate above, by unknown secondary synthesis processes, by local dynamical or sedimentation anomalies, or by some combination of these effects. Since we have at this time no evidence for special chemical or dynamical conditions at haze altitudes, we proceed to explore condensation in some detail.

Nature and Abundance of Organic Products

There is substantial evidence that energy sources active in the Titanian atmospheric environment naturally lead to the formation of an array of organic compounds ranging to high molecular masses. In early irradiations of CH_4/N_2 atmospheres, performed in the context of the origin of life, high molecular mass products up to some 900 Da were detected (Balestic, 1974). In proton bombardment experiments, aliphatic hydrocarbons up to C_{22} have been reported (Scattergood and Owen, 1977). Pyrolytic GC/MS of the solid organic tholins produced on sparking CH_4/NH_3 mixtures detects some 50 separate organic compounds (Khare *et al.*,



FIG. 6. The abundance of simple organics as a function of heavy atom number for a variety of laboratory simulation experiments, for terrestrial biogenic and suspected abiogenic sediments, and for Titan observations and photochemical models. The slopes of these curves yield the abundance parameter α , used in computing Figs. 8–11. Sample values of α (reference slopes) are shown at lower right.

1981a). Pyrolytic GC/MS analysis of tholins prepared in a Titan atmosphere simulation indicates >75 compounds (Khare et al., 1982). The Titan tholins, which match the observed properties of the clouds (Sagan and Khare, 1981, 1982; Khare et al., 1981b; Sagan et al., 1983; Thompson et al., 1984), presumably form from simpler intermediates resembling their pyrolyzates, and release these constituents on irradiation. Thus, with a wide variety of simple and complex organic molecules expected in the atmosphere of Titan, each characterized by its own vapor pressure curve, we anticipate condensation at many levels in the atmosphere. Do the condensation levels of some common organic products correspond to the observed altitudes of Titan haze and cloud?

The study of the condensation of products of general atmospheric organic synthesis requires an estimate of the abundance of the various chemical species synthesized. Since abundances have been measured directly for only a small subset of these compounds (Table 1), estimated abundances, based on the results of laboratory simulation experiments, must be used for the many intermediate molecular mass products which we consider. We approach this problem by estimating the rate at which molecular abundance falls with increasing heavy atom number, a parameter whose common logarithm we define as α . In Fig. 6 we plot, for various simulation experiments and for organics in terrestrial sediments. the relative mole fraction of organic products versus the heavy atom (C + N) number. The slope of these log-log curves is α . Also plotted are segments of the observed curves for Titan. We see from Fig. 6 that ultraviolet irradiation at $\lambda < 1550$ Å, electrical discharge, and energetic electron bombardment of CH₄ or CH₄/N₂ mixtures at a wide variety of pressures yields $0.25 \leq \alpha \leq$ Suspected abiogenic hydrocarbon 0.5. gases dissolved at great depth in Black Sea sediments give α between 0.3 and 1.0 (Hunt and Whelan, 1978). Only the Nonesuch shale hydrocarbons, which are probably bi-

ogenic, have values of α significantly less than those in simulation experiments, at least in the low heavy atom number range. The currently available data make the observed value of α for Titan similar to that in laboratory simulations. Comparable values emerge from the elaborate absolute reaction rate kinetics calculation of Titanian photochemistry of Yung et al. (1984), especially near altitudes of highest production rates. Pyrolyzates of CH₄/NH₃ tholins produced by long-wavelength UV or spark irradiation exhibit compounds with up to nine heavy atoms at abundances 10^{-1} to 10^{-2} of those of the most abundant effluents (Khare et al., 1978, 1981a)-tholin pyrolyzates exhibit values of α almost as small as for the Nonesuch shale. Similar conclusions apply for CH_4/N_2 tholins (Khare et al., 1982). Below, we compute condensation profiles for $\alpha = 0.0, 0.25, 0.5, \text{ and } 1.0,$ but expect that values $0.25 \leq \alpha \leq 0.5$ most nearly apply.

We consider those molecules detected by Voyager (Table I), some of the major and minor pyrolyzates of synthesis experiments for which extensive GC/MS analysis has been performed (Khare et al., 1981a), and a series of aliphatic hydrocarbons and aromatic ring systems. The estimated abundances are given by $X = X_0 \ 10^{-\alpha(n-n_0)}$. where X is the mole fraction, n the heavy atom number, and the zero subscript denotes a reference molecule. For each chemical class of molecules, this reference is the molecule from Table 1 judged most appropriate: for saturated hydrocarbons, C_3H_8 ; for alkenes, C_2H_4 ; for alkynes and aromatic rings, C₂H₂; for saturated nitriles, HCN; for dinitriles, C₂N₂; etc. For molecules having more than one functionality the smaller of the possible estimates is used. For $\alpha = 0$, X is calculated by the physically more reasonable assumption of constant mass fraction rather than mole fraction as a function of n.

Computation of Vapor Saturation Profiles

Saturation curves are constructed, em-

ploying standard values for heats of vaporization and fusion and at least one pressure-temperature reference point. In a single case (HC₃N) the heat of vaporization, and in some other cases (Appendix II) the heat of fusion, is estimated by comparison with a series of homologous compounds. The normal hydrocarbon and aromatic series are chosen as illustrative models for which vapor pressure data are readily available. Variation of the heats of vaporization (or sublimation) with temperature does not significantly affect the results and is not included. Condensation temperatures $T_{\rm c}$ as a function of atmospheric pressure p are given by

$$T_{\rm c} = [T_{\rm r}^{-1} - (R/\mu\Delta H) \ln(pX/p_{\rm r})]^{-1},$$

where T_r and p_r constitute a reference point in temperature-vapor pressure space, and R is the universal gas constant (in molar units), μ the molecular mass of the condensing molecule, ΔH the specific heat of vaporization or sublimation as appropriate, p the total atmospheric pressure, and X the mole fraction. Condensation occurs when the curve so constructed intersects the atmospheric structure curve $(T_{atm} \leq T_c)$. (Many of the organic compounds considered are to some extent mutually soluble. The presence of multicomponent solutions will generally lower the saturation vapor pressure of each component compound, and in many cases lead to condensation at altitudes slightly higher than those of the pure condensates, shown here.)

Altitudes and Quantities of Condensates

In Fig. 7 are vapor saturation temperature profiles for all the organic compounds detected by Voyager. [Condensation curves for some of these compounds were presented in Maguire *et al.* (1981).] Every one of them condenses far below the upper limits of the main cloud deck (~2825 km). Since CH₄ condenses at about 2615 km and all detected compounds condense below 2700 km, the upper portion of the main cloud deck must consist almost entirely of higher molecular mass molecules, both the



FIG. 7. Vapor saturation temperature profiles for Voyager-detected organic molecules in Titan's atmosphere. On each curve is shown the generic formula, name, and abundance of the condensate. The dashed curve shows the effect of lowering the C_3H_8 abundance to 5×10^{-6} . All detected compounds condense in the mid to lower clouds, below 2660 km.

organic condensates discussed here and sedimenting tholins.

Vertical optical depths τ_v of particulate condensates are estimated from the scattering cross section κ in the geometric limit:

$$\tau_{\rm v} = \kappa L_{\rm c} = \left[2\pi r^2 / (4\pi r^3 \rho/3)\right] (p/g) (\mu X/\bar{\mu}) f_{\rm c}$$
$$= 3\mu X p f_{\rm c} / 2\bar{\mu} g \rho r,$$

where L_c is the mass column density of condensate, ρ and r are particle density and radius, $\bar{\mu}$ is the mean atmospheric molecular mass, and f_c is the ratio of the quantity of compound in the condensed state to that observed in the gas state. We find

$$\tau_{v} = 5 \times 10^{5} \left(\frac{\mu}{\overline{\mu}}\right) X \left(\frac{p}{1 \text{ mb}}\right) f_{c}$$
$$\left(\frac{125 \text{ cm sec}^{-2}}{g}\right) \left(\frac{0.25 \ \mu\text{m}}{r}\right) \left(\frac{1 \text{ g cm}^{-3}}{\rho}\right).$$

The values $\rho \approx 1 \text{ g cm}^{-3}$ and $r \approx 0.25 \,\mu\text{m}$ apply at haze altitudes (Rages and Pollack, 1980). Particles sizes are expected to range to >1 μm at lower altitudes, in the main cloud deck (Toon *et al.*, 1980; Podolak *et*

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COLUMN DENSITIES AND OPTICAL DEPTHS OF KNOWN ATMOSPHERIC CONSTITUENTS^a

Compound	Density (g cm ⁻³)	Condensation pressure (mbar)	Column density (g cm ⁻²)	$\tau_{\rm v} \approx 3\mu X p f_{\rm v}/2\bar{\mu}\rho g r$
HC ₃ N	~1	16	1 × 10 ⁻⁵	0.2
HCN	0.69	18	3×10^{-5}	0.6
C_4H_2	0.74	20	8×10^{-6}	0.2
C_2N_2	0.95	22	2×10^{-5}	0.3
C_3H_8	0.59	28	7×10^{-3}	170
C_3H_4	0.71	29	9×10^{-6}	0.2
C_2H_2	0.62	32	4×10^{-4}	11
C_2H_6	0.57	45	7×10^{-3}	190
C₂H₄	0.65	140	4×10^{-4}	10
CH₄	0.45	- 1997	4×10^{-1}	13,000

^{*a*} Vertical optical depths are computed for 1- μ m particles in the geometric limit, and assume f_c = 1 (equal amounts of condensate and overlying gas). The actual value of f_c may be substantially less (see text). CH₄ column density and optical depth involve no assumption on f_c (Thompson and Sagan, 1984). C₂H₄ probably condenses, but its condensation curve is almost tangent to the temperature minimum (Fig. 7). Densities are from the *CRC Handbook of Chemistry and Physics* (Weast, 1980) except for CH₄ (Ramaprasad *et al.*, 1978), C₂H₄ (Ligthart *et al.*, 1979), and HC₃N (estimated).

al., 1984). If the particle and gas scale heights are comparable, the air mass for tangential observations is about 20, so a value of τ_v as small as 5×10^{-2} suffices to generate unit tangential optical depth in the condensate haze. The minimum optical depth for visibility is substantially less: the highest hazes detected have $\tau_v = 1 \times 10^{-2}$ at 2932 ± 5 km, with $r \approx 0.3 \ \mu$ m (Rages and Pollack, 1983).

It is clear that even the minor constituents shown in Fig. 7 can produce large optical depths of condensate in the main cloud deck. Vertical optical depths which would result from a mass density of $1-\mu m$ particles equal to that in the gaseous state $(f_c = 1)$ are shown in Table V. At these altitudes $(\sim 2650 \text{ km})$ the characteristic time for a 1- μ m particle to fall one scale height (H_0 = $RT/\bar{\mu}g \simeq 25$ km) is 3 years (Toon *et al.*, 1980). Comparable vapor and condensate mass density would be expected if the eddy diffusion time scale $t = H_0^2/K$ were about the same as this characteristic sedimentation time, i.e., if $K \simeq 5 \times 10^4$ cm² sec⁻¹. Large eddy diffusivities will increase the ra-

tio of condensate to vapor (and the condensate will be more dispersed), while smaller values of K will decrease f_c . The photochemical rate model of Smith et al. (1982b), based on C₂H₂ abundances observed by the Voyager EUV experiment, indicates $K \simeq$ 10^3 cm² sec⁻¹ at 2650 km; thus optical depths of major condensates at these lower altitudes may be substantially less than those computed assuming $f_c = 1$ as in Table V. Also included in Table V is the column density of CH₄, found by modeling the Voyager far-infrared spectrum (Thompson and Sagan, 1984), and its estimated optical depth (assuming again $1-\mu m$ particles in the geometric limit). The amount of CH₄ is much greater than the estimated column densities for the most abundant minor constituents detected by Voyager: 0.4 g cm⁻² for CH₄ versus 0.007 g cm⁻² for C_2H_6 and C_3H_8 (with $f_c = 1$). Thus, while the opacity of the upper cloud is observed to be substantial, and the optical depth at lower altitudes resulting from the condensation of Voyager-detected compounds is $\sim 10-100$, the optical depth of the CH₄ cloud in the



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upper troposphere is much larger still, $\sim 10^3$ -10⁴ for particle sizes 10 to 1 μ m, respectively.

There is a simple constraint on the altitude of the highest detectable haze: for condensation processes in which the abundance falls at least fast enough that the mass fraction is constant with molecular mass ($\mu X/\bar{\mu}$ = constant < 10⁻⁵), a detectable $\tau_{\rm v} \ge 1 \times 10^{-2}$ implies $p > 2 \times 10^{-3}$ mb. Thus no compounds present at mass fraction $< 10^{-5}$ will produce visible quantities of material above about 3060 km. Conversely the altitude of the highest detected haze at visible wavelengths (2932 km: Rages and Pollack, 1983) implies a mass fraction of haze $\simeq 6 \times 10^{-7} \simeq \mu X f_c / \bar{\mu}$. Unless special conditions of local production or transport exist, the presence of a condensate haze this high in the atmosphere itself implies an abundant suite of organic compounds of intermediate to high molecular mass.

In Figs. 8a–d we show the condensation levels for normal hydrocarbons, assuming the four values of α listed above, respectively. Using these aliphatic hydrocarbons as a model series, we see that observable hazes at the correct altitudes can be produced provided $\alpha \leq 0.5$. The substantial optical depth of the main cloud deck below ~2800 km also requires a decrease no faster than this. No compounds condense in adequate abundance to produce visible wavelength opacity above about 2670 km, i.e., anywhere in the upper clouds, if $\alpha \geq 1$ (Fig. 8d).

The C₃H₈ abundance of 2×10^{-5} (Maguire *et al.*, 1981) upon which all computed saturated hydrocarbon mole fractions are based, has recently be reestimated as 5×10^{-6} (R. E. Samuelson, 1983, personal communication). This new determination is itself model-dependent and rather uncertain, and should not be regarded as a definitive final figure. In Fig. 8a we show condensation curves based on the nominal value of 2×10^{-5} (solid lines) and on the lower estimate (dashed lines). Using the lower estimate reduces all hydrocarbon abundances

by a factor of 4 and shifts all the condensation profiles horizontally by -5 ± 1 K° at the altitudes of intersection with the atmospheric p-T profile; a lesser shift results at higher altitudes. These changes in abundances and altitudes are sufficiently small that, after noting the type and magnitude of the effect here and in Fig. 8a, we base further computed hydrocarbon mole fractions upon the original published C₃H₈ abundance. A reduction in the assumed abundance of C₃H₈ will affect only the condensation curves shown in Figs. 8b-d, and the two saturated hydrocarbons, n-butane and *n*-pentane, in Figs. 11a-d, producing shifts toward slightly lower temperatures in these cases very similar to those shown in Fig. 8a.

The results for a model based on representative aromatic ring systems are shown in Figs. 9a-d. If the production of higher molecular mass products is extensive (Figs. 9a,b), compounds condensing below about 3000 km can be seen, but those having more than about 10 heavy atoms, both for the aliphatic series (Figs. 8a,b) and for the aromatic series (Figs. 9a,b), will condense at higher altitudes-many at the level of production-and be mixed vertically as particulates rather than as gases. Members of the model ring series have a lower overall abundance since the reference molecule adopted as the base of abundance computations is C_2H_2 . For this series, generation of observable hazes at high altitudes requires $\alpha \leq 0.25$ (Fig. 9b).

In Figs. 10a–d we present vapor pressure curves for a few of the most abundant tholin pyrolyzates made in simulation experiments (Khare *et al.*, 1981a). These low molecular mass compounds condense at altitudes below 2700 km, in the main cloud deck. In order for them to contribute significant cloud opacity there, α must be ≤ 0.5 . Results for some lower abundance tholin GC/MS pyrozylates are shown in Figs. 11a–d. Again, if these compounds are to produce substantial opacity in and possibly above the main cloud deck, α must be ≤ 0.5 .



abundance models.





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DISCUSSION

Many of the molecules produced in greatest abundance in Titan's upper atmosphere condense at altitudes within and below the observable main cloud. Discrete hazes may be produced by the condensation of a single major compound, or of a group of compounds that condense at approximately the same altitude. Nearly all high molecular mass products synthesized at high altitude will condense *in situ*. These particles are subject to growth and sedimentation processes at all altitudes below the level of production (Toon *et al.*, 1980; Podolak and Podolak, 1980).

In all cases for which detectable hazes condense near 2900 km altitude, the heavy atom number appears to be around 9 or 10, and we are led to speculate that the detached limb hazes are composed of molecules with approximately this number of (C + N) atoms. The condensation of molecules with a particular number of heavy atoms at a particular altitude derives from a general correlation between molecular mass and vapor pressure, a correlation which is very systematic for the nonpolar classes of organic compounds (alkanes, alkenes, alkynes, nitriles) preferentially produced by energetic processes in an N₂/CH₄ atmosphere. Thus, because of its temperature structure, the atmosphere of Titan serves as a kind of fractional distillation device, condensing out simple organic molecules deep below the cloud tops, molecules of intermediate complexity near the cloud tops, and detached hazes and sedimenting compounds of still greater complexity at higher altitudes. The high molecular mass products condense at the altitudes of production, and contribute to the observed EUV opacity there.

To explain the detached limb hazes by such a fractional condensation mechanism requires, for most categories of molecules tested, that $\alpha \leq 0.5$. Ranges of α suggested by the relevant laboratory simulation experiments in which CH₄ or CH₄/N₂ mixtures are irradiated (Fig. 6) surround this value. It is then not implausible that the detached hazes are, at least in part, organic condensates of molecular mass 100 to 150 Da. We support the idea that condensation is indeed the cause of, or a necessary precursor to, the formation of the haze simply because there seems to be no other process which leads to the concentration of material in such a narrow altitude range (a few tens of kilometers).

We recognize at least four varieties of organic hazes or clouds in the atmosphere of Titan: (1) primary production, EUV-absorbing organic molecules chiefly in the range 3200 to 3600 km; (2) condensation hazes of primary production organic molecules localized in the limb hazes below 2940 km and in the main cloud deck; (3) tholins-formed both from the irradiation of atmospheric constituents [part of (1) above] and from the chemical processing of primary hazes, and distributed throughout the atmosphere-which serve as nucleation centers for condensation and impart UV and visible absorption to cloud particles; and (4) tropospheric $CH_4/C_2H_6/N_2$ clouds resulting from the evaporation and condensation of surface volatiles (Thompson and Sagan, 1984; Lunine et al., 1983).

The high-altitude hazes, which we identify with high molecular mass condensates mixed with dark nitrogenous organics similar to Titan tholin, have substantial UV opacity but much lower visible absorption (Caldwell *et al.*, 1981; Nelson and Hapke, 1978). These properties are basically consistent with the so-called "Axel dust" first proposed for Jupiter by Axel (1972), for the upper atmosphere of Titan by Danielson *et al.* (1973) and for Saturn by Macy (1973). We will report in a separate communication on a study of Jupiter and Saturn organic production and possible condensation.

Although the organic compounds condensing at haze and cloud altitudes are generally entirely transparent in the visible, the scattering optical depths for C_2H_6 , C_3H_8 , and especially CH_4 at visible wavelengths could easily be large enough to diffuse and render indistinguishable Titanian surface contrast through pure multiple scattering, even if the absorption by tholin is neglected.

While the two-stream radiative equilibrium model of Samuelson (1983) predicts a "red" optical depth ≈ 2 , the ratio of the scattering cross section in his "red" channel to that in the "violet" channel is unreasonably small (~1/150). As Samuelson himself notes, the vertical homogeneity required in his model is the likely cause for this disparity. We expect that the atmospheric scattering properties vary strongly with altitude, with absorbing materials, abundant at higher altitudes, scoured from the lower atmosphere by condensation processes. Since the scattering will then be very conservative, large optical depths (such as that computed to the CH_4 cloud in Table V) can be accommodated without eliminating the solar flux in the red and

Formula	Name	Reference for UV spectra
N ₂	Nitrogen	Cole and Dexter (1978) Gurtler <i>et al.</i> (1977)
³⁶ Ar	Argon	Hudson and Kieffer (1971)
CH₄	Methane	Koch and Skibowski (1971) Okabe and Becker (1963) Mount <i>et al</i> . (1977)
H ₂	Hydrogen	Lee et al. (1976) Cook and Metzger (1964)
H ₃ C—CH ₃	Ethane	Okabe and Becker (1963) Mount and Moos (1978)
H ₃ C-CH ₂ -CH ₃	Propane	Okabe and Becker (1963)
HC≡CH	Ethyne (acetylene)	Nakayama and Wantabe (1964)
$H_2C = CH_2$	Ethene (ethylene)	McDiarmid (1980) Wilkinson and Mulliken (1955)
HC≡N	Methanenitrile (hydrogen cyanide)	Nagata <i>et al.</i> (1981) Macpherson and Simons (1978)
НС≡С−С≡СН	Butadiyne (diacetylene)	Georgieff and Richard (1958) Lamotte <i>et al.</i> (1977)
H ₃ C−C≡CH	Propyne (methylacetylene)	Nakayama and Wantabe (1964)
HC≡C−C≡N	Propynenitrile (cyanoacetylene)	Connors et al. (1974)
N≡C−C≡N	Ethanedinitrile (cyanogen)	Connors et al. (1974)
CO ₂	Carbon dioxide	de Reilhac and Damany (1977) Cook <i>et al.</i> (1966) Greening and King (1976) Rabalais <i>et al.</i> (1971) Ogawa (1971)

APPENDIX I

SOURCES OF UV SPECTRA OF	TITAN ATMOSPHERIC CONSTITUENTS
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near-infrared, part of which must be transmitted to the surface in order to sustain the temperature profile of the lower atmosphere.

It is possible to make a rough estimate of the single scattering albedo of the lower cloud from the requirement (Samuelson, 1983) that $\sim 25\%$ of the solar flux in the red and near-infrared penetrates to the surface. In the limit of strong forward scattering, the fraction of the solar beam reaching the surface is $f = \exp[-(1 - \tilde{\omega}_0)\tau]$ where $\tilde{\omega}_0$ is the single scattering albedo. If $f \approx 0.25$ and we guess $r = 10 \ \mu m$ then $\tau = 10^3$ and $\bar{\omega}_0 =$ 0.9986. (Since multiple scattering does of course take place, the actual value of $\bar{\omega}_0$ will be substantially closer to 1 than this value.) Mie scattering calculations show that, for $r/\lambda \sim 10$, a value of the imaginary refractive index $n_i \approx 1.5 \times 10^{-5}$ is implied. The n_i of tholin is at its minimum of 4 \times 10^{-4} from 1.2 to 1.8 μ m (Khare *et al.*, 1984), while that of liquid CH₄ is $\sim 10^{-9}$ (Thompson et al., 1984). If the particles are homogeneous, the n_i of the mixture will be directly proportional to the volume fraction of tholin. A generous estimate of the maximum allowable fraction of Titan tholin in cloud particles is then $1.5 \times 10^{-5}/4 \times 10^{-4}$ \approx 4%. We consider this a strong upper limit, subject to substantial reduction. We are in the process (Thompson et al., 1984) of computing the reflection and surface transmission for Titan model atmospheres with gas, haze, and cloud in amounts indicated by Thompson and Sagan (1984). These calculations will define more precisely the transmission to the surface and allow a much better estimate of the tholin content of the tropospheric clouds.

The presence of a conservatively scattering upper tropospheric cloud of large optical depth is supported by the results of Podolak *et al.* (1984) and Podolak (1984), who find that a bright reflecting cloud near T_{min} is essential to explain the equivalent widths of the atmospheric CH₄ bands at 5430, 6190, and 7200 Å in their vertically inhomogeneous scattering model.

APPENDIX II

ESTIMATED HEATS OF FUSION OF ORGANIC COMPOUNDS⁴

Formula	Name	$\Delta H_{\rm f}$ (cal g ⁻¹)
CH ₂ CHCN	Propenenitrile	40
CH ₃ CH ₂ CN	Propanenitrile	35
C ₄ H ₈	1-Butene	30
C_4H_8	cis-2-Butene	30
C ₄ H ₈	trans-2-Butene	30
$(CH_2CN)_2$	Butanedinitrile	35
φCN	Benzonitrile	32
ϹΗ₃φϹ₂Η₅	3-Ethyltoluene	26
C₄H ₉ CN	Pentanenitrile	28
CH₃∳CN	p-Toluonitrile	32
C ₆ H ₁₂	1-Hexene	30
φCHCH ₂	Styrene	32
CH3CHCHCN	2-Butenenitrile	35
CH ₂ CH ₂	Ethene	33
CHCCN	Propynenitrile	40
¢CH₂∳	Diphenylmethane	30
¢₃CH	Triphenylmethane	30
$C_{13}H_{28}$	<i>n</i> -Tridecane	35.8
C ₁₄ H ₃₀	<i>n</i> -Tetradecane	53.4
$C_{15}H_{32}$	n-Pentadecane	37.5
C ₁₆ H ₃₄	n-Hexadecane	55.6
$C_{17}H_{36}$	<i>n</i> -Heptadecane	39.1
$C_{26}H_{54}$	n-Hexacosane	39.0

"Heats of fusion (ΔH_t) for linear hydrocarbons are derived by linear interpolation between the nearest available values for odd or even carbon number molecules, as appropriate—a permissible approach because of the smooth variation of the heats of fusion of the odd and even carbon number series, taken independently. For other molecules, we employ the ΔH_t values of those compounds, for which data are available, that are chemically and structurally most similar. These values are adjusted in some cases to take account of trends in the heats of fusion of a structurally similar series. For example, we adopt $\Delta H_t(n-C_8H_{16}) =$ $\Delta H_t(n-C_6H_{12}) + |\Delta H_t(n-C_8H_{18}) = \Delta H_t(n-C_6H_{14})|$.

Ultraviolet irradiation of organic ices at 77°K leads to the synthesis of organic molecules of greater complexity (Sagan and Khare, 1973). With a residence time of several years for 0.3- μ m particles above the main cloud deck (Toon *et al.*, 1980) the accumulated UV dose for a quantum yield of only 0.1 for $\lambda < 2000$ Å amounts to the breaking of every chemical bond several times over. Eventually, for example, through the production of polyenes, porphyrins, or polyaromatics, the condensates that originally had substantial opacity only in the UV begin to darken in the visible as well. It is possible that UV and other radiation-damaged condensates are an alternative path to the formation of visible chromophores in the Titanian atmosphere.

The mix of condensed ices and tholins, coagulating and sedimenting out of the Titanian atmosphere will provide a rich layer of liquid and solid organics at the surface. Given the expected dominance of low molecular mass organics in this layer, much of the product may remain in the liquid state (Lunine *et al.*, 1983), although significant amounts of organics will supersaturate and precipitate as sediment even if a surface ocean exists.

While the studies of Toon et al. (1980) and Podolak and Podolak (1980) concerned the coagulation, growth, and sedimentation of particles produced at high altitude only (corresponding to primary tholin products in this paper), and considered those as sufficient alone to explain Titan cloud properties, it would be surprising if there were not a suite of intermediate molecular mass organics bridging the gap between the observed synthetic products (molecular mass \leq 42) and hazes—not only the oligoacetylenes (Allen et al., 1980), but many of the products produced in laboratory simulations as well. We are therefore confident that Titan's clouds are characterized by some combination of the growth of tholin particles envisioned by Toon et al. (1980) and of the condensation of relatively abundant products of high energy synthesis which we have considered here. Our assertion that the Titan cloud particles are in fact mixtures of tholin and condensed intermediate molecular mass material (at all except the highest altitudes) is supported by the recent results of Podolak (1984) discussed previously, which indicate that both a very absorbing component of lower abundance (which we identify with nitrogenous

charged particle product) and a less absorbing component of higher abundance (which we identify with photochemical product) must be present in order simultaneously to explain the polarization, and brightness in the continuum and CH_4 absorption bands, of Titan's atmosphere.

Particle growth and sedimentation studies, including condensation of intermediate molecular mass products, and multiple light scattering studies, based on particles with n_i spectra relevant for Titan tholin, photochemical products, and mixtures of these components, will be illuminating paths of further enquiry.

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REFERENCES

- ALLEN, M., J. P. PINTO, AND Y. L. YUNG (1980). Titan: Aerosol photochemistry and variations related to the sunspot cycle. Astrophys. J. 242, L125– L128.
- ARVESEN, J. C., R. N. GRIFFIN, JR., AND B. D. PEAR-SON, JR. (1969). Determination of extraterrestrial solar spectral irradiance from a research aircraft. *Appl. Opt.* 8, 2215–2232.
- AXEL, L. (1972). Inhomogeneous models of the atmosphere of Jupiter. *Astrophys. J.* **173**, 451–468.
- BALESTIC, F. S. (1974). Synthèse Abiotique d'Acides Aminés par Voie Radiochimique. Doctoral thesis, Université Paris Sud, Orsay, France.
- BAR-NUN, A., AND M. PODOLAK (1979). The photochemistry of hydrocarbons in Titan's atmosphere. *Icarus* 38, 115-122.
- BROADFOOT, A. L., B. R. SANDEL, D. E. SHE-MANSKY, J. B. HOLBERG, G. R. SMITH, D. F. STRO-BEL, J. C. MCCONNELL, S. KUMAR, D. M. HUN-TEN, S. K. ATREYA, T. M. DONAHUE, H. W. MOOS, J. L. BERTAUX, J. E. BLAMONT, R. B. POMPHREY, AND S. L.INICK (1981). Extreme ultraviolet observations from Voyager 1 encounter with Saturn. Science 212, 206-211.
- CALDWELL, J. J. (1974). Ultraviolet observations of Titan from OAO-2. In *The Atmosphere of Titan* (D. M. Hunten, Ed.), NASA Special Publication SP-340. NASA, Washington, D.C.

- CALDWELL, J., T. OWEN, A. R. RIVOLO, AND V. MOORE (1981). Observations of Uranus, Neptune, and Titan by the International Ultraviolet Explorer. *Astron. J.* 86, 298–305.
- CAPONE, L. A., J. DUBACH, S. S. PRASAD, AND R. C. WHITTEN (1983). Galactic cosmic rays and N₂ dissociation on Titan. *Icarus* 55, 73–82.
- CAPONE, L. A., S. S. PRASAD, W. T. HUNTRESS, R. C. WHITTEN, J. DUBACH, AND K. SANTHANAM (1981). Formation of organic molecules on Titan. *Nature* **293**, 45–46.
- CHANG, S., T. SCATTERGOOD, S. ARONOWITZ, AND J. FLORES (1979). Organic chemistry on Titan. *Rev. Geophys. Space Phys.* **17**, 1923–1933.
- COLE, B. E., AND R. N. DEXTER (1978). Photoabsorption and photoionization measurements on some atmospheric gases in the wavelength region 50–340 Å. J. Phys. B 11, 1011–1023.
- CONNORS, R. E., J. L. ROEBBER, AND K. WEISS (1974). Vacuum ultraviolet spectroscopy of cyanogen and cyanoacetylenes. J. Chem. Phys. 60, 5011– 5024.
- COOK, G. R., AND P. H. METZGER (1964). Photoionization and absorption cross sections of H₂ and D₂ in the vacuum ultraviolet region. J. Opt. Soc. Amer. 54, 968–972.
- COOK, G. R., P. H. METZGER, AND M. OGAWA (1966). Absorption, photoionization, and fluorescence of CO₂. J. Chem. Phys. 44, 2935–2942.
- DANIELSON, R. E., J. J. CALDWELL, AND D. R. LARACH (1973). An inversion in the atmosphere of Titan. *Icarus* 20, 437–443.
- DF REILHAC, L., AND N. DAMANY (1977). Photoabsorption cross-section measurements of some gases, from 10 to 50 nm. J. Quant. Spectrosc. Radiat. Transfer 18, 121–131.
- GEORGIEFF, K. K., AND Y. RICHARD (1958). Diacetylene: Preparation, purification, and ultraviolet spectrum. *Canad. J. Chem.* 36, 1280–1283.
- GILLETT, F. C. (1975). Further observations of the 8– 13 micron spectrum of Titan. Astrophys. J. 201, L41–L43.
- GILLETT, F. C., W. J. FORREST, AND K. M. MERRILI (1973). 8–13 micron observations of Titan. Astrophys. J. 184, L93–L95.
- GREENING, F. R., AND G. W. KING (1976). Rydberg states of carbon dioxide and carbon disulfide. *J. Mol. Spectrosc.* **59**, 312–325.
- GUPTA, S., E. OCHIAI, AND C. PONNAMPERUMA (1981). Organic synthesis in the atmosphere of Titan. *Nature* **293**, 725–727.
- GURTLER, P., V. SAILE, AND E. E. KOCH (1977). High resolution absorption spectrum of nitrogen in the vacuum ultraviolet. *Chem. Phys. Lett.* **48**, 245–250.
- HANEL, R., B. CONRATH, F. M. FLASAR, V. KUNDE, W. MAGUIRE, J. PEARL, J. PIRRAGLIA, R. SAMUELSON, L. HERATH, M. ALLISON, D. CRUIK-SHANK, D. GAUTIER, P. GIERASCH, L. HORN, R.

KOPPANY, AND C. PONNAMPERUMA (1981). Infrared observations of the Saturnian system from Voyager 1. *Science* **212**, 192–200.

- HARRIS, D. L. (1961). Photometry and colorimetry of planets and satellites. In *Planets and Satellites* (G. P. Kuiper and B. M. Middlehurst, Eds.). Univ. of Chicago Press, Chicago.
- HEROUX, L., AND H. E. HINTEREGGER (1978). Aeronomical reference spectrum for solar UV below 2000 angstroms. J. Geophys. Res. 83, 5305– 5308.
- HUDSON, R. D., AND L. J. KIEFFER (1971). Compilation of Ultraviolet Photoabsorption Cross Sections for Atoms between 5 and 3500 Å, NASA Special Publication SP-3064. NASA, Washington, D.C.
- HUNT, J. M. (1979). Petroleum Geochemistry and Geology, p. 20. Freeman, San Francisco.
- HUNT, J. M., AND J. K. WHELAN (1978). Dissolved gases in Black Sea sediments. In *Initial Reports of Deep Drilling Project. Leg 42B* **42**, part 2 (D. A. Ross and Y. P. Neprochov, Eds.), pp. 661–665. U.S. Govt. Printing Office, Washington, D.C.
- HUNTEN, D. M. (1977). Titan's atmosphere and surface. In *Planetary Satellites* (J. A. Burns, Ed.). Chap. 20. Univ. of Arizona Press, Tucson.
- JULIUSSON, E. (1975). Composition of cosmic rays at 10¹⁰ to 10¹³ eV/nucleus. *14th International Cosmic Ray Conference: Conference Papers*, Vol. 8, pp. 2689–2698.
- KHARE, B. N., J. GRADIE, AND C. SAGAN (1981b). Reflection spectra of simulated Titan organic clouds. Bull. Amer. Astron. Soc. 13, 701.
- KHARE, B. N., AND C. SAGAN (1973). Red clouds in reducing atmospheres. *Icarus* 20, 311–321.
- KHARE, B. N., C. SAGAN, E. T. ARAKAWA, F. SUITS, T. A. CALLCOTT, AND M. W. WILLIAMS (1984). Optical constants of organic tholins produced in simulated Titanian atmospheres: From soft X-ray to microwave frequencies. *Icarus* 60, in press.
- KHARE, B. N., C. SAGAN, E. L. BANDURSKI, AND B. NAGY (1978). Ultraviolet-photoproduced organic solids synthesized under simulated Jovian conditions: Molecular analysis. *Science* 199, 1199–1201.
- KHARE, B. N., C. SAGAN, S. SHRADER, AND E. T. ARAKAWA (1982). Molecular analysis of tholins produced under simulated Titan conditions. *Bull. Amer. Astron. Soc.* 14, 714.
- KHARE, B. N., C. SAGAN, J. E. ZUMBERGE, D. S. SKLAREW, AND B. NAGY (1981a). Organic solids produced by electrical discharge in reducing atmospheres: Tholin molecular analysis. *Icarus* 48, 290– 297.
- KOCH, E. E., AND M. SKIBOWSKI (1971). Optical absorption of gaseous methane, ethane, propane, and butane and reflection of solid methane and ethane in the vacuum ultraviolet. *Chem. Phys. Lett.* **9**, 429– 432.
- KRIMIGIS, S. M., T. P. ARMSTRONG, W. I. AXFORD,

C. O. BOSTROM, C. Y. FAN, G. GLOECKLER, AND L. J. LANZEROTTI (1977). The low energy charged particle (LECP) experiment on the Voyager spacecraft. *Space Sci. Rev.* **21**, 329–354.

- KRIMIGIS, S. M., T. P. ARMSTRONG, W. I. AXFORD, C. O. BOSTROM, G. GLOECKLER, E. P. KEATH, L. J. LANZEROTTI, J. F. CARBARY, D. C. HAMILTON, AND E. C. ROELOF (1981). Low-energy charged particles in Saturn's magnetosphere: Results from Voyager 1. Science 212, 225–231.
- KRIMIGIS, S. M., T. P. ARMSTRONG, W. I. AXFORD, C. O. BOSTROM, G. GLOECKLER, E. P. KEATH, L. J. LANZEROTTI, J. F. CARBARY, D. C. HAMILTON, AND E. C. ROELOF (1982). Low-energy hot plasma and particles in Saturn's magnetosphere. *Science* 215, 571–577.
- KUIPER, G. P. (1944). Titan: A satellite with an atmosphere. Astrophys. J. 100, 378-383.
- KUNDE, V. G., A. C. AIKIN, R. A. HANEL, D. E. JENNINGS, W. C. MAGUIRE, AND R. E. SAMUELSON (1981). C_4H_2 , HC_3N and C_2N_2 in Titan's atmosphere. *Nature* **292**, 686–688.
- LAMOTTE, J., C. BINET, AND R. ROMANET (1977). N° 81—Structure vibrationelle des spectres d'absorption ultraviolettè de quelques hydrocarbures α -diyniques et homologues deutèriès. J. Chim. Phys. Chim.-Biol. 74, 577–585.
- LEE, L. C., R. W. CARLSON, AND D. L. JUDGE (1976). The absorption cross sections of H₂ and D₂ from 180 to 780 Å. J. Quant. Spectrosc. Radiat. Transfer 16, 873–877.
- LIGTHART, F. A. S., N. J. TRAPPENIERS, AND K. O. PRINS (1979). Nuclear magnetic resonance in solid ethylene at high pressure: 1. The phase diagram of solid ethylene at high pressure. *Physica B* + C (*Am-sterdam*) **97**, 172–186.
- LIN, R. P., K. A. ANDERSON, AND T. L. CLINE (1972). Detection of interplanetary electrons from 18 keV to 1.8 MeV during solar quiet times. *Phys. Rev. Lett.* **29**, 1035–1038.
- LUNINE, J. L., D. J. STEVENSON, AND Y. L. YUNG (1983). Ethane ocean on Titan. *Science* **222**, 1229– 1230.
- LUTZ, B. L., C. DE BERGH, AND T. OWEN (1983). Titan: Discovery of carbon monoxide in its atmosphere. *Science* 200, 1374–1375.
- MACPHERSON, M. T., AND J. P. SIMONS (1978). Spectroscopic study of the predissociation H(D)CN $(\tilde{C}^{1}A') \rightarrow$ H(D) + CN($B^{2}\Sigma^{+}$). J. Chem. Soc. Faraday II 74, 1965–1977.
- MACY, W. W., JR. (1973). Inhomogeneous Models of the Atmosphere of Saturn. Doctoral thesis, Princeton University, Princeton, N.J.
- MAGUIRE, W. C., R. A. HANEL, D. E. JENNINGS, V. G. KUNDE, AND R. E. SAMUELSON (1981). C_3H_8 and C_3H_4 in Titan's atmosphere. *Nature* **292**, 683–686.
- MAGUIRE, W.C., R. HANEL, D. JENNINGS, R. SAMUELSON, A. AIKIN, AND Y. YUNG (1982). CO₂

on Titan. Presented at the Saturn Conference, Univ. of Arizona, 14 May 1982.

- MCDIARMID, R. (1980). A reinvestigation of the absorption spectrum of ethylene in the vacuum ultraviolet. J. Phys. Chem. 84, 64–70.
- MEYER, P. (1969). Cosmic rays in the galaxy. Annu. Rev. Astron. Astrophys. 7, 1–38.
- MOUNT, G. H., AND H. W. MOOS (1978). Photoabsorption cross sections of methane and ethane, 1380-1600 Å, at T = 295 K and T = 200 K. Astrophys. J. 224, L35-L38.
- MOUNT, G. H., E. S. WARDEN, AND H. W. MOOS (1977). Photoabsorption cross sections of methane from 1400 to 1850 Å. Astrophys. J. 214, L47–L49.
- MOYER, B. J. (1958). Instruments for measuring radiation. In *Nuclear Engineering Handbook* (H. Etherington, Ed.), Chap. 5. McGraw-Hill, New York.
- NAGATA, T., T. KONDOW, Y. OZAKI, AND K. KU-CHITSU (1981). Absorption spectra of hydrogen cyanide and deuterium cyanide in the 130–80 nm range. *Chem. Phys.* 57, 45–53.
- NAKAYAMA, T., AND K. WANTABE (1964). Absorption and photoionization coefficients of acetylene, propyne, and 1-butyne. J. Chem. Phys. 40, 558-561.
- NELSON, R. M., AND B. W. HAPKE (1978). Spectral reflectivities of the Galilean satellites and Titan, 0.32 to 0.86 micrometers. *Icarus* **36**, 304–329.
- NESS, N. F., M. H. ACUNA, K. W. BEHANNON, L. F. BURLAGA, J. E. P. CONNERNEY, R. P. LEPPING, AND F. M. NEUBAUER (1982). Magnetic field studies by Voyager 2: Preliminary results at Saturn. *Science* 215, 558–563.
- OGAWA, M. (1971). Absorption cross sections of O_2 and CO_2 continua in the Schumann and far-uv regions. J. Chem. Phys. 54, 2550–2555.
- OKABE, H. (1978). Photochemistry of Small Molecules. Wiley, New York.
- OKABE, H., AND D. A. BECKER (1963). Vacuum ultraviolet photochemistry. VII. Photolysis of n-butane. J. Chem. Phys. 39, 2549–2555.
- Owen, T. (1982). The composition and origin of Titan's atmosphere. *Planet. Space Sci.* **30**, 839–848.
- PODOLAK, M. (1984). Are the polarization data consistent with constant flux models of Titan's atmosphere? *Icarus* 58, 325–329.
- PODOLAK, M., A. BAR-NUN, N. NOY, AND L. P. GIVER (1984). Inhomogeneous models of Titan's aerosol distribution. *Icarus* 57, 72–82.
- PODOLAK, M., AND E. PODOLAK (1980). A numerical study of aerosol growth in Titan's atmosphere. *Icarus* 43, 73–84.
- RABALAIS, J. W., J. M. MCDONALD, V. SCHERR, AND S. P. MCGLYNN (1971). Electronic spectroscopy of isoelectronic molecules: II. Linear triatomic groupings containing sixteen valence electrons. *Chem. Rev.* 71, 73–108.
- RAGES, K., AND J. B. POLLACK (1980). Titan aerosols:

Optical properties and vertical distribution. *Icarus* **41**, 119–130.

- RAGES, K., AND J. B. POLLACK (1983). Vertical distribution of scattering hazes in Titan's upper atmosphere. *Icarus* 55, 50–62.
- RAMAPRASAD, K. R., J. CALDWELL, AND D. S. MC-CLURE (1978). The vibrational overtone spectrum of liquid methane in the visible and near infrared: Applications to planetary studies. *Icarus* 35, 400–409.
- RAULIN, F., A. BOSSARD, G. TOUPANCE, AND C. PON-NAMPERUMA (1979). Abundance of organic compounds photochemically produced in the atmospheres of the outer planets. *Icarus* 38, 358–366.
- RAULIN, F., D. MOUREY, AND G. TOUPANCE (1982). Organic synthesis from CH_4-N_2 atmospheres: Implications for Titan. *Orig. Life* **12**, 267–279.
- SAGAN, C. (1971). The solar system beyond Mars: An exobiological survey. *Space Sci. Rev.* 11, 73–112.
- SAGAN, C. (1973). The greenhouse of Titan. *Icarus* 18, 649–656.
- SAGAN, C. (1974). Organic chemistry in the atmosphere. In *The Atmosphere of Titan* (D. M. Hunten, Ed.), NASA Special Publication SP-340. NASA, Washington, D.C.
- SAGAN, C., AND S. L. DERMOTT (1982). The tide in the seas of Titan. *Nature* 300, 731–733.
- SAGAN, C., AND B. N. KHARE (1973). Experimental interstellar organic chemistry: Preliminary findings. In *Molecules in the Galactic Environment* (M. Gordon and L. Snyder, Eds.), pp. 399–408. Wiley, New York.
- SAGAN, C., AND B. N. KHARE (1981). The organic clouds of Titan. Bull. Amer. Astron. Soc. 13, 701.
- SAGAN. C., AND B. N. KHARE (1982). The organic clouds of Titan. Orig. Life 12, 280.
- SAGAN, C., AND W. R. THOMPSON (1984). Lifetime and replenishment processes for Titan's atmospheric methane. In preparation.
- SAGAN, C., W. R. THOMPSON, AND B. N. KHARE (1983). Reflection spectra of model Titan atmospheres and aerosols. *Bull. Amer. Astron. Soc.* 15, 843.
- SAMUELSON, R. E. (1983). Radiative equilibrium models of Titan's atmosphere. *Icarus* 53, 364–387.
- SAMUELSON, R. E., R. A. HANEL, V. G. KUNDE, AND W. C. MAGUIRE (1981). Mean molecular weight and hydrogen abundance of Titan's atmosphere. *Nature* 292, 688–693.
- SCATTERGOOD, T., P. LESSER, AND T. OWEN (1975). Production of organic molecules in the outer solar system by proton irradiation: Laboratory simulations. *Icarus* 24, 465–471.
- SCATTERGOOD, T., AND T. OWEN (1977). On the sources of ultraviolet absorption in spectra of Titan and the outer planets. *Icarus* **30**, 780–788.
- SMITH, B. A., L. SODERBLOM, R. BATSON, P. BRIDGES, J. INGE, H. MASURSKY, E. SHOEMAKER, R. BEEBE, J. BOYCE, G. BRIGGS, A. BUNKER, S. A.

Collins, C. J. Hansen, T. V. Johnson, J. L. Mitchell, R. J. Terrile, A. F. Cook II, J. Cuzzi, J. B. Pollack, G. E. Danielson, A. P. Ingersoll, M. E. Davies, G. E. Hunt, D. Morrison, T. Owen, C. Sagan, J. Veverka, R. Strom, and V. E. Suomi (1982a). A new look at the Saturn system: The Voyager 2 images. *Science* **215**, 504–537.

- SMITH, B. A., L. SODERBLOM, R. BEEBE, J. BOYCE, G. BRIGGS, A. BUNKER, S. A. COLLINS, C. J. HAN-SEN, T. V. JOHNSON, J. L. MITCHELL, R. J. TER-RILE, M. CARR, A. F. COOK II, J. CUZZI, J. B. POL-LACK, G. E. DANIELSON, A. INGERSOLL, M. E. DAVIES, G. E. HUNT, H. MASURSKY, E. SHOE-MAKER, D. MORRISON, T. OWEN, C. SAGAN, J. VEVERKA, R. STROM, V. E. SUOMI (1981). Encounter with Saturn: Voyager 1 imaging science results. Science 212, 163-190.
- SMITH, G. R., D. F. STROBEL, A. L. BROADFOOT, B. R. SANDEL, D. E. SHEMANSKY, AND J. B. HOLBERG (1982b). Titan's upper atmosphere: Composition and temperature from the EUV solar occultation results. J. Geophys. Res. 87, 1351-1360.
- STONE, E. C., R. E. VOGT, F. B. MCDONALD, B. J. TEEGARDEN, J. H. TRAINOR, J. R. JOKIPH, AND W. R. WEBBER (1977). Cosmic ray investigation for the Voyager missions; energetic charged particle studies in the outer heliosphere—And beyond. *Space Sci. Rev.* 21, 355–376.
- STROBEL, D. F. (1974). The photochemistry of hydrocarbons in the atmosphere of Titan. *Icarus* 21, 466– 470.
- STROBEL, D. F. (1982). Chemistry and evolution of Titan's atmosphere. *Planet. Space Sci.* 30, 839–848.
- STROBEL, D. F., AND D. E. SHEMANSKY (1982). EUV emission from Titan's upper atmosphere: Voyager 1 encounter. J. Geophys. Res. 87, 1361–1368.
- THOMPSON, W. R., AND C. SAGAN (1984). Titan: Farinfrared and microwave remote sensing of methane clouds and organic haze. *Icarus*, in press.
- THOMPSON, W. R., C. SAGAN, S. W. SQUYRES, AND B. N. KHARE (1984). Titan: Multiple light scattering analysis of Voyager data. In preparation.
- TOON, O. B., R. P. TURCO, AND J. B. POLLACK (1980). A physical model of Titan's clouds. *Icarus* **43**, 260–282.
- TOUPANCE, G., F. RAULIN, AND R. BUVET (1975). Formation of prebiochemical compounds in models of the primitive Earth's atmosphere: 1. CH_4-NH_3 and CH_4-N_2 atmospheres. *Orig. Life* **6**, 83–90.
- TRAFTON, L. M. (1972). The bulk composition of Titan's atmosphere. Astrophys. J. 175, 295–306.
- TYLER, G. L., V. R. ESHLEMAN, J. D. ANDERSON, G. S. LEVY, G. F. LINDAL, G. E. WOOD, T. A. CROFT (1981). Radio science investigations of the Saturn system with Voyager 1: Preliminary results. *Science* 212, 201–206.
- VAN ALLEN, J. A., M. F. THOMSEN, B. A. RANDALL, R. L. RAIRDEN, and C. L. GROSSKRENTZ (1980). Sa-

turnian trapped radiation and its absorption by satellites and rings: The first results from Pioneer. *Science* **207**, 411–421.

VERVERKA, J. (1973). Titan: Polarimetric evidence for an optically thick atmosphere? *Icarus* 18, 657-660.

- VOGT, R. E., D. L. CHENETTE, A. C. CUMMINGS, T. L. GARRARD, E. C. STONE, A. W. SCHARDT, J. H. TRAINOR, N. LAL, AND F. B. MCDONALD (1981). Energetic charged particles in Saturn's magnetosphere: Voyager 1 results. *Science* 212, 231-234.
- VOGT, R. E., D. L. CHENETTE, A. C. CUMMINGS, T. L. GARRARD, E. C. STONE, A. W. SCHARDT, J. H. TRAINOR, N. LAL, AND F. B. MCDONALD (1982). Energetic charged particles in Saturn's magnetosphere: Voyager 2 results. *Science* 215, 577-582.

WEAST, R. C. (Ed.) (1980). CRC Handbook of Chem-

istry and Physics, 61st ed. CRC Press, Boca Raton, Fla.

- WILKINSON, P. G., AND R. S. MULLIKEN (1955). Far ultraviolet absorption spectra of ethylene and ethylene-d₄. J. Chem. Phys. 23, 1895–1907.
- WOLFE, J. H., J. D. MIHALOV, H. R., COLLARD, D. D. MCKIBBIN, L. A. FRANK, AND D. S. INTRILIGA-TOR (1980). Preliminary results on the plasma environment of Saturn from the Pioneer 11 plasma analyzer experiment. Science 207, 403-407.
- YUNG, Y. L., M. ALLEN, AND J. P. PINTO (1984). Photochemistry of the atmosphere of Titan: Comparison between model and observations. Astrophys. J. Suppl. 55, 465–506.
- ZELLNER, B. (1973). The polarization of Titan. *Icarus* **18**, 661–664.