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ORGANIC CHEMISTRY ON TITAN

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ABSTRACT

Observations of nonequilibrium phenomena on the Saturn satellite Titan indicate the occurrence of organic chemical evolution. Greenhouse and thermal inversion models of Titan's atmosphere provide environmental constraints within which various pathways for organic chemical synthesis are assessed. Experimental results and theoretical modeling studies suggest that the organic chemistry of the satellite may be dominated by two atmospheric processes: energetic-particle bombardment and photochemistry. Reactions initiated in various levels of the atmosphere by cosmic ray, "Saturn wind," and solar wind particle bombardment of a CH_4 - N_2 atmospheric mixture can account for the C_2 -hydrocarbons, the uv-visible-absorbing stratospheric haze, and the reddish color of the satellite. Photochemical reactions of CH_4 can also account for the presence of C_2 -hydrocarbons. In the lower Titan atmosphere, photochemical processes will be important if surface temperatures are sufficiently high for gaseous NH_3 to exist. Hot H-atom reactions initiated by photo-dissociation of NH_3 can couple the chemical reactions of NH_3 and CH_4 , and are estimated to produce organic matter at a rate of about 10^{-13} to 10^{-14} $\text{g cm}^{-2} \text{ s}^{-1}$. Electric discharges are highly improbable on Titan; if they occurred at all, they would be restricted to the lower atmosphere. Their yield of organic matter might approach that of hot H-atom reactions if the conversion of solar to electrical discharge energy on Titan was as efficient as on Earth.

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I. INTRODUCTION

Two fundamental observations make the satellite Titan an object of great interest to exobiologists and organic cosmochemists: the unique occurrence of abundant methane (CH_4) in the atmosphere (Trafton, 1972) unaccompanied by higher amounts of H_2 (Münch *et al.*, 1977) and the presence of a reddish "surface" (Morrison and Cruikshank, 1974). Although there is some doubt in interpreting this surface as the top of a cloud layer or as the actual surface of the satellite, it does exist and its implications are significant for chemical evolution in the atmosphere. Interpretation of spectroscopic (Caldwell, 1974; Trafton, 1975), and polarimetric (Veverka, 1973; Zellner, 1973) observations of Titan indicate the existence of a thick particle layer in the atmosphere that absorbs ultraviolet and visible light, a layer characterized as a "photochemical haze" (Danielson *et al.*, 1973; Podolak and Danielson, 1977). Ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2) (Gillett, 1975) are attributable to, but should not be uniquely identified with, stratospheric CH_4 photochemical reactions (Strobel, 1974). In the context of Lewis' (1971) physical and chemical model of Titan, the presence of C_2H_6 , C_2H_2 , and C_2H_4 , the red surface, and a particle layer that absorbs ultraviolet and visible light clearly indicate a chemical nonequilibrium in the atmosphere. To the organic cosmochemist, this indicates reactions that yield organic molecules in a prebiotic environment perhaps related to those of primitive Earth (Sagan, 1974) and the parent bodies of carbonaceous meteorites. In turn, this draws the interest of exobiologists to the possibility that life may have originated or that terrestrial organisms may survive on Titan.

Recently, Margulis *et al.* (1977) discussed the models that have been proposed for Titan's atmosphere and their implications for life. No basis now exists to alter their conclusion that "the likelihood of growth of a terrestrial microbe is vanishingly small." By implication, the probability of the origin of life forms resembling terrestrial organisms on Titan is also "vanishingly small." If organisms with biochemistry fundamentally different from those of terrestrial organisms evolved and populate Titan today, there are no obvious methods for detecting and identifying them except, perhaps, by imaging techniques.

Rather than addressing a highly speculative issue such as Titan exobiology, in this paper, we discuss several more fundamental issues concerning the satellite's organic chemistry. Current models of Titan's atmosphere described in Section II will be used to help identify the nature and distribution of possible sources of organic matter. Data from the literature and this laboratory will be used to assess the rele-

vance and productivity of those sources as well as to characterize the nature of the products derived from them. The upper and lower atmospheres will be treated separately in Sections III and IV, respectively. A summary of our conclusions is presented in Section V.

II. WORKING MODELS OF THE ATMOSPHERE

Observations of Titan have provided support for two types of thermal atmosphere models. In the temperature-inversion model (Danielson *et al.*, 1973; Podolak and Danielson, 1977; Caldwell, 1977, 1978) the surface temperature (<100 K) and pressure (≤ 20 mbar) are low, but absorption of ultraviolet and visible sunlight by a high particle layer heats the upper atmosphere to as high as 160 K. In the greenhouse model (Sagan, 1973; Pollack, 1973; Cess and Owen, 1973; Hunten, 1978) the stratospheric temperature is also high as a result of dust particles, but it decreases with depth to a CH_4 cloud. Below this cloud, the temperature increases with depth to the surface where there are high temperatures (>150 K) and pressures (≥ 300 mbar). Podolak and Giver (1978) point out that with available data, it is not possible to distinguish the "surface" of the inversion model from the top of a thick dust-covered cloud layer below which a massive greenhouse atmosphere might prevail. Radio measurements by Briggs (1974) at 8085 MHz suggest a surface temperature of 135 ± 45 K, which is consistent with the inversion model as well as some greenhouse models. Microwave data of Conklin *et al.* (1977) favor a massive atmosphere with a pressure of several bars at the surface and a corresponding temperature near 260 K, although more recent data indicate that the temperature is closer to 100 K, consistent with the earlier measurements (Owen, 1978). These observations conflict in supporting a greenhouse model. Nonetheless, for any such model, the low H_2 concentrations observed by Münch *et al.* (1977) indicate that a different gas must drive the greenhouse. Nitrogen may fulfill this purpose (Hunten, 1972, 1978; Owen and Cess, 1975).

For purposes of discussion, we shall view the Titan atmosphere as a composite model with the following features taken from various sources: (1) a stratospheric dust layer that absorbs ultraviolet and visible sunlight; (2) a stratospheric temperature of 160 K decreasing to <100 K at the top of a thick, dust-covered, reddish cloud layer consisting primarily of hydrocarbon ices; (3) CH_4 or CH_4 and N_2 comprise the bulk of the atmospheric gases above and below the cloud layer; (4) a clear atmosphere from the bottom of the clouds at >100 K to the surface where the temperature is about 135 K

and the pressure about one bar; (5) NH_3 abundances below the clouds are determined by its vapor pressure at the surface either in the form of $\text{NH}_3 - \text{H}_2\text{O}$ ice or aqueous NH_3 solution.

III. UPPER ATMOSPHERE

Several factors must be reconciled about the chemistry of the upper atmosphere: evidence for C_2H_6 , C_2H_4 , and C_2H_2 as minor constituents, with a $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ ratio of about 250 (Gillett, 1975); evidence for dust particles that strongly absorb ultraviolet and visible light; and the red color of the observable surface.

Dust and Acetylene Polymerization

The dust particles are thought to be "photochemical smog" arising from CH_4 photolysis (Strobel, 1974). Scattergood and Owen (1977) suggested that a component of the dust particles might be a yellowish acetylene polymer, similar to cuprene $(\text{C}_2\text{H}_2)_n$, formed by particle or photo-induced polymerization of C_2H_2 , or both. Although polymers are routinely formed during the photolysis and thermal decomposition of C_2H_2 , the conditions on Titan may not support such processes.

Plasma polymerization of acetylene (Kobayashi *et al.*, 1974), alone and in the presence of saturated (C_2H_6) and unsaturated (C_2H_4) hydrocarbons readily occurs at pressures as low as 0.7 mbar to yield gaseous oligomers and solid polymers. The presence of H_2 in the gas mixture, however, partially inhibits polymerization. The solid polymers are insoluble and appear to consist of a highly cross-linked, three-dimensional network containing carbon-carbon double bonds and aromatic structures. It is not clear whether or not these polymers are closely related to the polymers identified as $(\text{C}_2\text{H}_2)_n$ produced during radiation-induced gas-phase polymerizations of C_2H_2 (Jones, 1959), because the infra-red spectra are dissimilar in many respects. Ultraviolet irradiation of pure C_2H_2 at 1470 Å (McNesby and Okabe, 1964) and 1849 Å (Zelikoff and Aschenbrand, 1956) also yields an ill-characterized solid polymer with smaller amounts of diacetylene ($\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$), vinylacetylene ($\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$), ethylene and benzene. At 1849 Å, quantum yields for C_2H_2 disappearance and the apparent chain length of polymers decrease with decreasing pressure. While these

polymers form readily under many conditions through many different energy sources (Jones, 1959; Lind, 1961, Kobayashi, 1974) their chemical constitutions are not uniquely defined; they are described, however, as near-white to yellowish and as lacking color-depth.

Recent laboratory studies provide the bases for assessing the possible existence of acetylene polymers on Titan. As a model for interstellar organic synthesis, Floyd *et al.* (1973) bombarded a solid film of C_2H_2 at 55 K with 150-eV electrons. They reported evidence for a variety of unsaturated and aromatic compounds, all of which are ultraviolet absorbers from 2000 - 3000 Å (Table 1). No mention was made of a solid cuprene-like product, although such a product would have been interesting in the context of interstellar organic chemistry. If polymers were absent, Floyd's work reveals an important temperature dependence for polymer formation, because previous polymer syntheses were achieved at room temperature or higher. Polymer synthesis on Titan may be inhibited by the low temperature of the stratosphere.

Recent experiments by Scattergood (1975), Flores *et al.* (1978) and Bar-Nun (1975, 1978) provide stronger additional arguments against the formation of solid acetylene polymers on Titan. Bombardment of gaseous CH_4 , C_2H_2 , and $CH_4 - C_2H_2$ mixtures with Mev protons (Scattergood, 1975) produced a yellowish powdery polymer in pure C_2H_2 and in mixtures of CH_4 and C_2H_2 where the CH_4/C_2H_2 ratio was < 2 . Clear, colorless liquids consisting primarily of simple saturated hydrocarbons resulted when the ratio was raised to 10. Apparently, under highly favorable total pressure conditions, a low mixing ratio of C_2H_2 in CH_4 prohibits formation of solid-colored polymer. We conclude that the CH_4/C_2H_2 ratio on Titan, which is estimated to exceed 10 by at least several orders of magnitude (Gillett, 1975; Strobel, 1974), also would be prohibitively high for C_2H_2 polymer synthesis by proton bombardment.

When 2.6 mbar of pure CH_4 is photolyzed with 1236 Å light (Flores *et al.*, 1978), the major products are the saturated hydrocarbons C_2H_6 and C_3H_8 (see Figure 1). After 30% CH_4 decomposition, when the system approached a photochemical steady-state, no hydrocarbons higher than C_4 were observed by gas chromatography, even when the total product was concentrated into a small volume by liquid nitrogen prior to sampling (Table 2). Not only did hydrocarbon production terminate at the C_4 stage, synthesis of unsaturated compounds was inhibited. These results essentially agree with experiments performed by Bar-Nun (1978). At the H_2/C_2H_2 ratio of 40 produced by CH_4 decomposition, the secondary process of C_2H_2 photopolymerization to a solid polymer is expected to be inhibited (Bar-Nun, 1975, 1978). Bar-Nun (1978) also found

Table 1. Ultraviolet Absorption Properties of Compounds Synthesized by 150 eV Electron Bombardment of C_2H_2 Films at 55 K

Compound	$\lambda_{\max} \text{ \AA}^a$	$\log \epsilon^a$
Diacetylene (HC_4H)	2340	-
Benzene (C_6H_6)	2030	2.5
	2540	3.9
Phenylacetylene ($C_6H_5C_2H$)	2350	4.2
	2720	2.5
Naphthalene ($C_{10}H_8$)	2200	5.0
	2750	3.8
Indene (C_9H_8)	2490	4.1

^aData taken from Hirayama (1965).

during irradiation of C_2H_2 that production of photopolymers decreased with lowerings of temperature and initial acetylene pressure below 300 K and 260 mbar, respectively. If the experimental data are extrapolated to Titan, and if CH_4 were the only hydrocarbon in the initial atmosphere, then the combined effects of low C_2H_2 mixing ratio, high H_2/C_2H_2 ratio, substantially lower temperatures, and pressures orders of magnitude lower would make photochemical formation of an acetylene polymer like $(C_2H_2)_n$ highly unlikely in the Titan stratosphere. This conclusion is consistent with the region

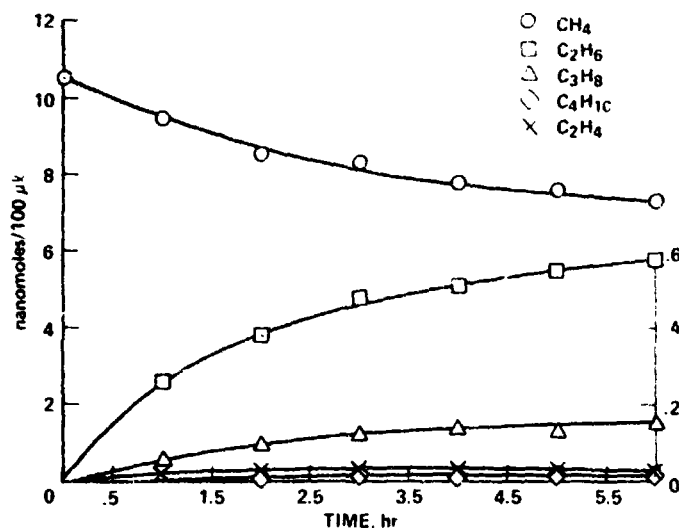


Figure 1. Product distributions at various times by irradiation of 2.6 mbar of CH_4 with 1236 Å light. Hydrocarbon abundances were determined by gas chromatography and are given in nanomoles per 100 μl sample. Left scale, CH_4 , right scale, other gases.

Table 2. Mole Fractions and Quantum Yields of Products Obtained by
1236 Å Irradiation of 2.6 mbar CH₄ at 200 K^a

Product	Mole Fraction ^b	Molecules Photon ^{-1c}
CH ₄	0.699	0.56 ^d
C ₂ H ₂	0.0016	0.0002
C ₂ H ₄	0.0048	0.014
C ₂ H ₆	0.107	0.15
C ₃ H ₆	0.0003	
C ₃ H ₈	0.0228	0.03
i - C ₄ H ₁₀	0.0019	
n - C ₄ H ₁₀	0.0021	0.001 ^e
H ₂	0.162	

^a Performed in a stirred 2196-cm³ flask with an Ophos lamp emitting $(6 \pm 2) \times 10^{15}$ photons s⁻¹.

^b Includes H₂ abundance calculated by mass balance. Mole fractions apply to near steady-state condition after 30% CH₄ decomposition.

^c Calculated at 10% CH₄ decomposition, unless otherwise specified. Errors estimated at $\pm 30\%$.

^d Molecules of CH₄ destroyed per absorbed photon.

^e Calculated when first observed, after 18% CH₄ decomposition.

^f Calculated for 30% CH₄ decomposition.

of CH₄-photolysis occurring at levels in the atmosphere corresponding to number densities of 10^9 to 10^{12} cm⁻³. Furthermore, the planetary data of Gillett (1975) and Münch *et al.* (1977) indicate a C₂H₂/CH₄ ratio $< 10^{-5}$ and an H₂/C₂H₂ ratio $< 10^4$.

Although synthesis of acetylene polymers in Titan's atmosphere is improbable, their contribution to the stratospheric dust cannot be ruled out. However, they certainly cannot account for Titan's reddish surface. On the other hand, ultraviolet absorbance by these polymers is assured by their double-bond and aromatic-ring content. Interestingly, electron micrographs of polymer produced by alpha-particle irradiation of C₂H₂ show them to consist of 0.1 to 0.13 μm-diameter spheres. As candidates for the photochemical smog, if they form in a low pressure medium, these particles conveniently remain solid at the relatively high stratospheric temperatures (150 K) postulated for both the inversion and greenhouse models, and are of the proper size to satisfy recent albedo (haze) models (Podolak and Giver, 1978).

High-Energy Particle Chemistry

If cuprene-like polymers at most comprise a minor component of the dust, what is the bulk of it? Apparently, the photochemistry of CH_4 alone cannot produce colored material. The products observed experimentally (Table 2) cannot account for even the observed absorption of ultraviolet light in Titan's stratosphere. Scattergood and Owen (1977) pointed out that production of colored material would require the presence of a nitrogen gas such as N_2 along with CH_4 . According to the working models, gases like NH_3 and H_2S cannot be involved because they become frozen below the stratosphere.

For purposes of comparison, the ultraviolet-visible and infrared spectra of condensable materials produced during Mev-proton irradiation of gas mixtures are shown in Figures 2 and 3. Table 3 contains a list of the major types of products. For N-containing mixtures, the spectra are similar and resemble those of the colored product obtained by 2537 Å irradiation of $\text{NH}_3 - \text{H}_2\text{S} - \text{CH}_4 - \text{C}_2\text{H}_6 - \text{H}_2\text{O}$ mixtures (Khare and Sagan, 1973). Because not one of these materials has spectral properties identical to those on Titan, Scattergood and Owen (1977) proposed that mixtures of materials similar to the $\text{CH}_4 - \text{H}_2$ and $\text{CH}_4 - \text{N}_2$ products were present. This is an attractive alternative because the components in appropriate proportions, more readily than the Khare-Sagan polymer alone, would permit the rapid increase in absorption toward the ultraviolet that is exhibited by dust in Titan's stratosphere (see Danielson *et al.*, 1973). Therefore, production of dust having the observed spectroscopic properties requires the coupling of C and N in a $\text{CH}_4 - \text{N}_2$ atmosphere.

From the incident proton energies of 2 Mev (with 0.75 Mev absorbed by the gas) and fluxes of $1.7 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ used in his experiments and estimates of the total CH_4 decomposition (based on decreases in infrared absorption), Scattergood (1975) calculated that $1.7 \times 10^4 \text{ CH}_4$ molecules per proton are converted to product (equivalent to 44 eV per CH_4). Coupling this figure with Titan's cosmic ray energy flux of $2.3 \times 10^9 \text{ eV cm}^{-2} \text{ s}^{-1} \text{ ster}^{-1}$ (Capone, 1978) leads to an estimated CH_4 loss rate of $5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ or production of $1.3 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$ of colored, condensable, carbonaceous matter. With this estimate, we assume that conversion of kinetic energy to chemical energy in the laboratory experiments is similar to that in Titan's lower ionosphere, despite orders of magnitude differences in flux density and total pressure. Assuming condensable matter with density of one is produced at a constant rate, $7.6 \times 10^{16} \text{ s}$ or $3 \times 10^3 \text{ y}$ would be required to deposit a 1- μm -thick layer of dust. After $4.5 \times 10^9 \text{ y}$, the total column density would be about 180 g cm^{-2} . Maximum energy deposition occurs around the 10^{18} cm^{-3} level of the atmosphere (Capone, 1978).

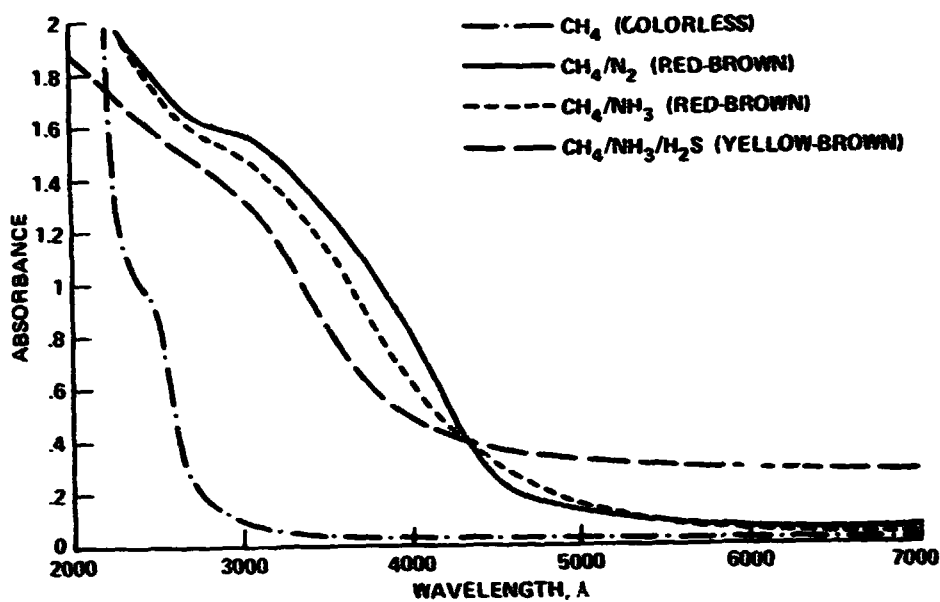


Figure 2. Ultraviolet-visible absorption spectra of liquid-phase products synthesized by MeV-proton irradiation of gas mixtures (Scattergood et al., 1975; Scattergood, 1975; Scattergood and Owen, 1977).

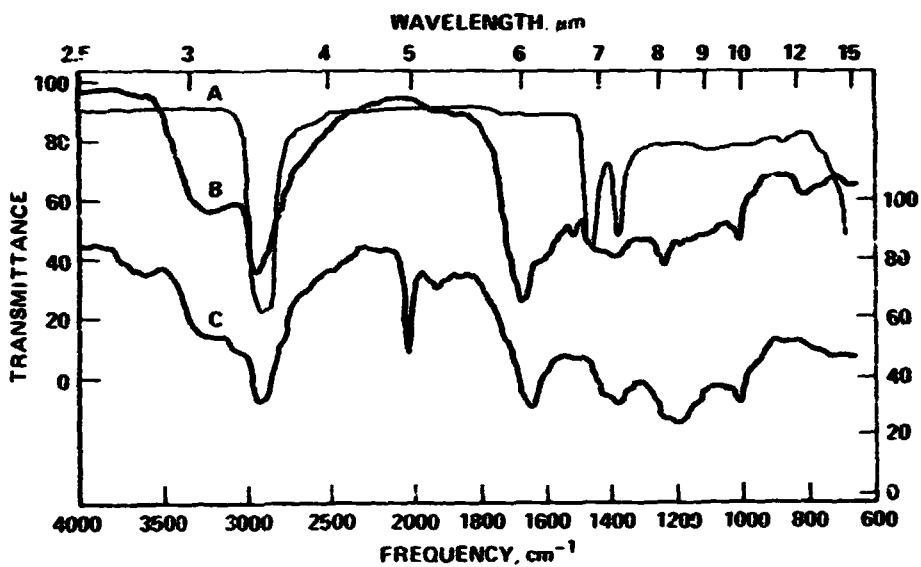


Figure 3. Infrared transmission spectra of liquid phase products obtained from MeV proton irradiation of gas mixtures: A. $\text{CH}_4 - \text{H}_2$; B. $\text{CH}_4 - \text{N}_2$ and $\text{CH}_4 - \text{NH}_3$; C. $\text{CH}_4 - \text{NH}_3 - \text{H}_2\text{S}$ (from Scattergood et al., 1975; Scattergood, 1975; Scattergood and Owen, 1977). Plot for mixture C is offset for clarity.

Recent calculations of Siscoe (1978) provide models for the magnetosphere associated with various possible values of Saturn's magnetic field. For a value as low as 0.5 gauss, the magnetosphere would extend to twenty Saturn radii and include Titan within its boundary 90% of the time. As a consequence of a $1.7 \text{ cm}^{-2} \text{ s}^{-1}$ particle density and a 200 km s^{-1} particle velocity, the flux of 150-eV "Saturn wind" protons striking the upper atmosphere of Titan would amount to $3.4 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. Calculated as above, these figures lead to an organic matter production rate at least twice that afforded by cosmic rays. Because of the shallow depth to which 150-eV protons can penetrate, consequent reactions should occur above the stratosphere in the region of maximum photochemistry, unlike the cosmic rays that penetrate deeper.

If Titan has no magnetic field, if the solar wind energy (avg, 1 keV nucleon⁻¹) and particle flux ($2 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$) are unaffected by Saturn's proximity, and if the assumptions given above for the production rate resulting from cosmic ray particles are applied, then an upper estimate can be made for the rate of synthesis of condensable carbonaceous matter by solar wind bombardment of the atmosphere. This estimate amounts to $1.1 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$ and is comparable to the cosmic ray production rate.

Table 3. Products Resulting from MeV Proton Irradiation of Various Gas Mixtures²

Gas mixture	
$\left. \begin{array}{l} \text{CH}_4 \\ \text{CH}_4 - \text{H}_2 \end{array} \right\}$	Aliphatic hydrocarbons ^b
$\left. \begin{array}{l} \text{CH}_4 - \text{N}_2 \\ \text{CH}_4 - \text{NH}_3 \end{array} \right\}$	$\left[\begin{array}{l} \text{Aliphatic hydrocarbons}^b \\ \text{Aliphatic and alicyclic amines}^c \\ \text{Acetonitrile (CH}_3\text{CN)} \\ \text{Red-brown polymer} \end{array} \right.$

^a From Scattergood (1975); Scattergood *et al.* (1975); Scattergood and Owen (1977).

^b Includes saturated and unsaturated compounds up to C₂₂ in length. Less than 10 ppm aromatics (e.g., benzene).

^c Cyclic amines include hexamethylenetetramine (C₆H₁₂N₄) and its methyl and dimethyl homologues.

Clearly, the assumptions used to obtain these estimates require that they be used with caution. Nonetheless, the role of particle radiation in producing condensable and gaseous trace constituents in Titan's atmosphere cannot be dismissed. Models of CH₄-rich atmospheres, which included cosmic ray ionization processes (Capone *et al.*, 1976), predicted CH₃ radical concentrations that were three orders of magnitude higher than those predicted by strictly photochemical models (Strobel, 1974). Because attainment of higher CH₃ concentrations without significantly lowering the I₃/H radical ratios is expected to favor a high hydrocarbon production, the predictions support the view that particle irradiation would enhance organic synthesis.

Electrical Discharges

In addition to synthesis of C₂H₂ polymers by way of CH₄ photolysis and synthesis of condensable organic matter by particle irradiation of CH₄ - N₂ mixtures, vacuum ultraviolet photolysis of CH₄ - N₂ or electric discharges may generate Titan's stratospheric dust and coloration. Electric discharges through CH₄ - N₂ mixtures at 36 mbar produce many different saturated and unsaturated hydrocarbons and nitriles (Toupance *et al.*, 1974) that could subsequently undergo photochemistry and condensation-polymerization reactions to readily form reddish substances if formed in Titan's atmosphere. To account for the occurrence of stratospheric dust in the absence of strong atmospheric mixing, however, electrical discharges must occur above the dust layer at pressures < 1 mbar in a dry atmosphere containing no clouds. Although they could conceivably occur, discharges under such conditions are sufficiently implausible as to permit discounting them.

Photochemistry

In the only report describing the coupling of C and N in the photochemistry of a CH₄ - N₂ mixture, Dodonova (1966) found that irradiations at 7 - 10 mbar with a hydrogen lamp (10¹⁵ - 10¹⁶ photons s⁻¹) produced HCN after 8 - 10 hr; hydrocarbons comprised the other products. HCN was detected with a picrate color test sensitive to 10⁻⁵ g. The explanation given for this result was "the photoactivation of nitrogen and its interaction with CH radicals resulting from the decomposition of methane." The author described that the photoactivation of nitrogen occurred at 1273 Å. A crude estimate based on the reported data places the quantum yield for HCN at about 10⁻⁵.

Although several attempts were made at NASA Ames Research Center (Bragin and Nicoll, 1976) to duplicate the Russian work with a 1236 Å lamp, they failed to produce any HCN detectable by high sensitivity gas-chromatographic analyses. If formed on Titan by Lyman- α photons at the estimated yield, however, HCN would be produced at the insignificant rate of about $10^3 \text{ cm}^{-2} \text{ s}^{-1}$ or $4.5 \times 10^{-8} \text{ g cm}^{-2} \text{ s}^{-1}$. Further attempts to study the photochemistry of $\text{CH}_4 - \text{N}_2$ at Lyman- α and other wavelengths would be desirable because gaseous HCN is photochemically converted to more complex organic compounds and reddish-brown solids (Mizutani *et al.*, 1975).

Thus, the most attractive mechanism for production of stratospheric dust on Titan that we have discussed involves high-energy proton irradiation, which requires a $\text{CH}_4 - \text{N}_2$ atmosphere. This source could provide the colored condensates that are responsible for the reddish surface of the satellite and its low ultraviolet-visible albedo. Unless vacuum ultraviolet photolysis of $\text{CH}_4 - \text{N}_2$ yields HCN more efficiently than 10^{-5} molecules per photon, it can be discounted along with electric discharges as a tenable mechanism.

If we now return to the data for 1236 Å photolysis of CH_4 (see Figure 1, Table 2), we can make additional observations pertinent to Titan's atmospheric photochemistry. Although a photochemical steady-state had not been reached at the time of measurement of the mixing ratios in Table 2, it was sufficiently close (see Figure 1) that the assumption of steady-state is justified. The relative abundances of experimental products suggest that propane (C_3H_8) may also be detectable in Titan's atmosphere along with the previously observed ethane (C_2H_6) and acetylene (C_2H_2). This idea has also been proposed by Bar-Nun and Podolak (1978). Propane should actually be more abundant than C_2H_2 . On the other hand, C_2H_2 should be the least abundant of these hydrocarbons. The experimental $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ ratio of 0.050 is lower by a factor of 10 than the ratio predicted by the CH_4 -photochemical model of Strobel (1974). Furthermore, the ratio of quantum yields for C_2H_4 and C_2H_6 point to an experimental $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio of 0.045, which is 10 - 100 times the ratio obtained in the model calculations. Although spectroscopic observations do not provide a useful measure of the $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ ratio, they do indicate a $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio of 4×10^{-3} (Gillett, 1975), consistent with the CH_4 -photolysis calculations. Clearly, there are difficulties in duplicating planetary environments in computer and laboratory simulations of CH_4 photolysis. Whether these difficulties may account for the discrepancies between the results of the simulations remains to be evaluated.

IV. LOWER ATMOSPHERE

Recently, Woodman *et al.* (1977) established an upper limit of 30 cm-am for the abundance of ammonia on Titan. In the context of the inversion model described in Section II, low surface temperatures of < 100 K remove essentially all NH_3 from the gas phase by condensation. As the temperature reaches 115 K, however, gas-phase NH_3 photochemistry can occur, as we discuss below. Because of the ambiguity about the nature of the Titan surface and the possible range of surface temperatures measured by radio (135 ± 45 K, Briggs, 1974) and microwave (260 K, Conklin *et al.*, 1977) observations, we considered ammonia photolysis at temperatures ranging from 115 to 200 K. If the "surface" of the inversion model corresponds to the actual surface, a temperature of 115 K implies that pure solid CH_4 is unlikely to be a major surface constituent. If the surface is the top of a cloud layer, the 115 K implies cloud particles that consist of hydrocarbons other than CH_4 or possibly NH_3 . Photolysis at >115 K is considered to occur in the atmosphere below the clouds of the greenhouse models.

Ammonia Photochemistry

Although Huntén (1973) discussed NH_3 photolysis as a means for generating large amounts of N_2 on Titan, the process has not been modeled for Titan. In theoretical studies of Jovian atmospheric chemistry, NH_3 and CH_4 photolysis reactions are decoupled from each other (Prinn, 1970; Strobel, 1973a, 1973b; Prasad and Capone, 1976). Except in the work of Kuhn *et al.* (1977), production of organic compounds by means other than CH_4 photolysis high in the stratosphere is discounted. However, laboratory experiments (Sagan and Khare, 1973; Becker *et al.*, 1974; Ferris and Chen, 1975; Ferris *et al.*, 1977) suggest that hot H atoms generated by photodissociation of NH_3 or H_2S (or both) can initiate reactions with CH_4 and C_2H_6 to produce organic compounds by way of hydrocarbon radicals such as CH_3 and their recombination with each other and with NH_2 radicals. Data in Table 4 summarize results reported by Ferris *et al.* (1977) and include estimated production rates at Titan obtained by extrapolation of their results. The product yields in the 115 K experiment were based on an experimental quantum yield for NH_3 decomposition of 0.12 at 208 K (Nicodem and Ferris, 1973). In the low-temperature experiments, some NH_3 is considered and the gas-phase abundances of NH_3 correspond to the equilibrium vapor pressures. Entries in the bottom two lines of Table 4 show that from 115 - 347 K photolysis of ammonia is accompanied by induced hot-atom decomposition of CH_4 at levels higher than 0.6 CH_4

Table 4. Photolysis of a Mixture of H₂ (0.623 bar), He (0.080 bar), CH₄ (0.125 bar), and NH₃ (0.040 bar) with 1849 Å Light at Various Temperatures: Product Yields and Estimated Production Rates at Titan^a

Product	Product Yield (molecules/photon)			Estimated Production Rate at Titan ^b (g cm ⁻² s ⁻¹)
	347 K	200 K	115 K	
H ₂	0.67			
N ₂	0.14	0.040	0.007	0.93 × 10 ⁻¹²
N-organics ^c	0.02	0.04	0.103	1.0 × 10 ⁻¹²
HCN	1.2 × 10 ⁻⁴	0.94 × 10 ⁻⁴	0.79 × 10 ⁻⁴	2.1 × 10 ⁻¹⁵
C ₂ H ₆	2.3 × 10 ⁻⁴			
C ₃ H ₈	0.59 × 10 ⁻⁴			
C ₄ H ₁₀ + C ₄ H _x	0.59 × 10 ⁻⁵			
C ₅ H _y	0.5 × 10 ⁻⁷			
N ₂ H ₄	1.7 × 10 ⁻⁶	0.56 × 10 ⁻³	1.09 × 10 ⁻⁵	1.5 × 10 ⁻¹⁴
(NH ₃ loss)	(0.30)	(0.12)	(0.12)	(0.6 × 10 ¹¹ cm ⁻² s ⁻¹) ^d
(CH ₄ loss)	(0.25)	(0.073)	(0.083)	(0.4 × 10 ¹¹ cm ⁻² s ⁻¹) ^d

^aProduct yields calculated from data of Ferris *et al.* (1977), using quantum yields for NH₃ photolysis obtained at 347 K (Ferris *et al.*, 1977) and 208 K (Nicodem and Ferris, 1973).

^bCalculated from yields at 200 K using a photon flux of 2 × 10¹² cm⁻² s⁻¹ between 1600 - 2270 Å at Titan divided by 4.

^cAssumed to be CH₃NH₂; other possibilities may include NH₂CN, CH₃CN, NH₂NHCH₃.

^dColumn photodecomposition rate.

molecule per NH_3 molecule dissociated. Furthermore, photolytic losses of CH_4 and NH_3 cannot be accounted for by summing the observed products. This lack of mass balance undoubtedly results in part from the difficulty of the analyses. Also, other compounds not specifically sought were likely to have evaded detection.

Mass balance for nitrogen requires the formation of the "N-organics" designated in Table 4. Methylamine (CH_3NH_2) with a N/C ratio of 1 and molecular weight 31 is taken to represent these compounds. Early on, Becker and Hong (1977) detected CH_3NH_2 in similar experiments, but not after long irradiations. Apparently, facile conversion of CH_3NH_2 to other compounds under the irradiation conditions accounts for its absence in most experiments. Formation of complex and colored organic matter from HCN or CH_3NH_2 or both by secondary photolytic processes can be readily envisioned. Mass balance for carbon also indicates the formation of more hydrocarbons than are reported in Table 4. Using the data for 200 K, and assuming that the missing carbon is in the form of $(\text{CH}_2)_n$, a hydrocarbon production rate of $0.4 \times 10^{-12} \text{ g cm}^{-2} \text{ s}^{-1}$ is required for mass balance. The total production rate of organic matter from NH_3 photochemistry and hot hydrogen-atom chemistry amounts to $1.4 \times 10^{-12} \text{ g cm}^{-2} \text{ s}^{-1}$. At this rate, a 1- μm -thick layer of organic matter (with unit density) would take about eight days to produce on Titan, and 4.5×10^9 yr of production would yield a 2-km-thick layer of organic matter and liberate 10^3 km-am of N_2 (or a column density of 28×10^{26} molecules cm^{-2}). Even if only 0.1% of the photons from 1600 - 2270 Å penetrated the cloud layer of Titan, the production of organic matter and N_2 would be significant.

The 115 and 200 K experiments of Table 4 represent relevant laboratory simulations of organic photochemistry on Titan. In greenhouse models, 115 K may occur at the top of the cloud layer, within it, or at some level below it. The high CH_4 partial pressure of this experiment, however, disqualifies its relevance to the inversion model. The 200 K temperature corresponds to a level somewhere below the clouds of the greenhouse models, either at or above the surface. The presence of H_2 and He are also relevant, not because they exist on Titan at the experimental abundances, but because they represent agents for collisional thermalization of the hot H atom. On Titan, N_2 may be the thermalizing agent. However, H_2 and He are expected to be more efficient thermalizers than N_2 (Wolfgang, 1963).

Hot Hydrogen Atom Chemistry

To explore hot atom chemistry under other possible planetary conditions, Aronowitz *et al.* (1978) developed a novel use of a computational method. Their approach couples hot-atom chemistry with the general kinetic problem by incorporating the kinetic theory of Wolfgang (1963) for hot atoms. Temperature, pressure, and incident photon energy are explicitly taken into account. A complete discussion of the approach is beyond the scope and intent of this report, however, and will appear in full detail elsewhere (Aronowitz *et al.*, 1978).

In these computations, the photochemistry is approximated in the following manner. An assemblage of molecules corresponding to an atmospheric composition is exposed to an arbitrarily chosen total number of photons in a series of incremental steps. A small fraction of the available NH_3 is dissociated by each increment of photons; the resulting primary products, H (hot) and NH_2 are allowed to interact with each other and with other gas components in the system according to the reactions in Table 5. The resulting mole fractions of reactants (e.g., NH_3) and products (e.g., N_2H_4) are determined iteratively. The calculations are allowed to run to the point at which additional iterations have negligible effect on the mole fractions of stable end products. The photodissociation of NH_3 was kept low ($\leq 5\%$) by limiting the number of photons introduced in the calculations. For purposes of simplification, the quantum yield for NH_3 was assigned a value of 1.0 for all wavelengths. Use of an appropriate scaling factor, however, permits correction of the calculated quantum yields for any photodissociation quantum yield < 1.0 . Secondary photolysis of products is neglected. Quantum yields obtained for various products were calculated from the number of photons and the mole fractions of products. The simulated environmental parameters and derived quantum yields are listed in Table 6. In each experiment, the NH_3 partial pressure is governed by its equilibrium vapor pressure (estimated from a fitted equation of the Antoine form) at the indicated temperature. These estimates are smaller than those determined by Gulkis *et al.* (1976) and hence constitute a lower bound on the NH_3 abundance.

Data in Table 6 reveal several interesting aspects of hot-atom chemistry over the range of conditions simulated. Under all conditions, C_2H_6 and CH_3NH_2 are formed, and CF_3NH_2 is the dominant product. With temperature and wavelength constant, total pressure increases (Experiments I, II, III) lead to increased CH_4

Table 5. Reactions Pertinent to Ammonia Photolysis and Hot Atom Chemistry on Titan

Reaction	Rate Constant ^a	Reference
(1) $\text{H}(\text{hot}) + \text{H}_2 \rightarrow \text{H}(\text{thermal}) + \text{H}_2$	Calculations used hot atom theory	
(2) $\text{H}(\text{hot}) + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$	Calculations used hot atom theory	
(3) $\text{H}(\text{hot}) + \text{NH}_3 \rightarrow \text{H}_2 + \text{NH}_2$	Calculations used hot atom theory	
(4) $2\text{H}(\text{thermal}) + \text{M} \rightarrow \text{H}_2 + \text{M}$	$2.9 \times 10^{15} (300/\text{T})^{0.6}$	Ham <i>et al.</i> , 1970 ^b
(5) $\text{H}(\text{thermal}) + \text{CH}_3 \rightarrow \text{CH}_4$	2.3×10^{14}	Cheng <i>et al.</i> , 1977
(6) $\text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}$	$2.2 \times 10^{19} (\text{M})$	Dodd and Steacie, 1954 ^b
(7) $\text{H}(\text{thermal}) + \text{NH}_2 \rightarrow \text{NH}_3$	1.8×10^{13}	Boyd <i>et al.</i> , 1971 ^b
(8) $\text{NH}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{NH}_2$	6.6×10^{13}	Kuhn <i>et al.</i> , 1977
(9) $\text{NH}_2 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_4$	1.5×10^{13}	Pham Van Khe <i>et al.</i> , 1977

^aThe rate constants are in units of $\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$ for two body and $\text{cm}^6 \text{mole}^{-2} \text{s}^{-1}$ for three body reactions.

^bFrom Strobel (1973a), Table 4.

decomposition, which is also reflected in higher yields of C_2H_6 . Formation of CH_3NH_2 appears to be favored by lower pressure. Lowering the temperature from 155 to 125 K (Experiments II, IV) causes little change in the product yields. Quantum yields for CH_4 decomposition decrease as the irradiating wavelength increases (Experiments V, II, VI). This decrease occurs because the hot H atoms produced at longer wavelengths are less energetic ("hot"). The influence of H_2 as a thermalizing agent is striking (Experiments IX, XI). When the H_2/CH_4 ratio is high, CH_4 and NH_3 decomposition are inhibited, and recombination of CH_3 and NH_2 radicals with thermalized H atoms takes place. As a result of inefficient production of CH_3 radicals by hot H atoms, substantially diminished yields of C_2H_2 and CH_3NH_2 occur. Excess N_2 exerts no influence on the thermalization of hot H atoms (Experiments II, IX). However, when the model calculations permit inelastic rather than elastic collisions of the

Table 6. Calculated Quantum Yields for Consumption of Reactants and Formation of Products by Hot-Atom Reactions Under Various Titan Conditions

Experiment	CH ₄ /H ₂ /N ₂ /NH ₃ (mole ratios)	T, P (K, bar)	λ(Å)	Quantum Yields (molecules/photon)				
				-NH ₃	-CH ₄	N ₂ H ₄	C ₂ H ₆	CH ₃ NH ₂
I.	1/1/1/[6.7(-6)]	125, 0.022	1850	0.996	0.913	0.128	0.087	0.740
II.	1/1/1/[2.9(-7)]	125, 0.526	1850	0.984	0.926	0.266	0.237	0.452
III.	1/1/1/[1.1(-7)]	125, 1.316	1850	0.977	0.932	0.340	0.217	0.298
IV.	1/1/1/[1.6(-3)]	155, 0.526	1850	0.986	0.925	0.249	0.218	0.489
V.	1/1/1/[2.9(-7)]	125, 0.526	1686	0.986	0.956	0.279	0.264	0.428
VI.	1/1/1/[2.9(-7)]	125, 0.526	2014	0.980	0.875	0.265	0.213	0.449
VII.	100/1/1/[2.2(-4)]	125, 0.022	1850	0.999	0.998	0.064	0.063	0.872
VIII.	100/1/1/[9.5(-6)]	125, 0.526	1850	0.999	0.999	0.305	0.305	0.389
IX.	1/1/400/[3.8(-5)]	125, 0.526	1850	0.984	0.926	0.266	0.237	0.452
X. ^a	1/1/400/[3.8(-5)]	125, 0.526	1850	0.482	0.141	0.194	0.024	0.094
XI.	1/100/400/[4.8(-5)]	125, 0.526	1850	0.371	0.018	0.180	0.003	0.011

^aSame as IX except calculations provided for inelastic collisions between N₂ and the hot atoms.

hot H atom with N_2 (Experiment X), quantum yields for CH_4 decomposition and C_2H_6 and CH_3NH_2 synthesis drop by factors of 7, 10, and 5, respectively.

Over the range of conditions tested by the model calculations, changes in temperature, total pressure and irradiating wavelength cause relatively small variations in the yields of products. The presence of high abundances of the moderating gases N_2 and H_2 (e.g., $CH_4/N_2 \leq 0.003$) reduces the yields by up to one order of magnitude. Although H_2 is a more effective thermalizer than N_2 , its abundance on Titan is not expected to exceed that of CH_4 (Münch *et al.*, 1977). Conditions of 125 K and 22 mbar (total pressure) represent the closest experimental simulation of the surface environment in the inversion model. Other simulations correspond to locations below the clouds of the greenhouse models.

To estimate production rates on Titan from the data in Table 6, a value of 0.12 for the quantum yield of NH_3 photodissociation is assumed. This value was measured at 208 K in excess H_2 ($H_2/NH_3 = 749$) by Nicodem and Ferris (1973), who found its magnitude had increased from a value of 0.04 at 313 K. This inverse correlation with temperature suggests that the value of 0.12 may be a lower limit below 208 K. For conditions that apply to atmospheric levels above the clouds, transmission of 10% of the incident sunlight is assumed; below the clouds, 1% transmission is assumed. Product quantum yields at 1850 Å are taken to represent average yields from 1600 - 2270 Å. The resulting total production rates of hot atom products corresponding to various conditions are listed in Table 7. Production rates based on the experimental data of Table 4 are also included as the bottom two lines, and are in reasonable agreement with theoretical results.

If the surface temperature of the inversion model were 125 K, a 1 μ m layer of organic matter would accumulate every 46 days, leading to a 360-m-thick layer after 4.5×10^9 yr. Organic synthesis occurs at 115 K and may extend to even lower temperatures provided that some NH_3 exists in the gas phase. The possibility of hot-atom-mediated synthesis in the solid phase at low temperature remains to be evaluated. If the lowest production rate in Table 7 is taken to represent synthesis below the clouds of greenhouse models, then settling of products to the surface would yield a 1 μ m-thick layer after 900 yr and a 5-m layer after 4.5×10^9 yr.

Table 7. Production Rates for Organic Matter Synthesized by Ammonia Photolysis and Hot H-Atom Chemistry Under Various Simulated Titan Conditions

CH ₄ /H ₂ /N ₂ /NH ₃ (mole ratios)	Experiment (Table VI)	T, P (K, bar)	Production Rates ^a	
			(mole. cm ⁻² s ⁻¹)	(g cm ⁻² s ⁻¹)
1/1/1/ 6.7(-6)	(I)	125, 0.022	5.0 × 10 ¹⁰	2.5 × 10 ⁻¹³
1/1/1/ 1.1(-7)	(III)	125, 1.316	3.1 × 10 ¹⁰	1.6 × 10 ⁻¹⁴
1/1/1/ 1.6(-3)	(IV)	155, 0.526	4.3 × 10 ¹⁰	2.1 × 10 ⁻¹⁴
100/1/1/ 2.2(-4)	(VII)	125, 0.022	5.6 × 10 ¹⁰	2.8 × 10 ⁻¹³
1/1/400/ 3.8(-5)	(X)	125, 0.526	0.7 × 10 ¹⁰	0.35 × 10 ⁻¹⁴
0.2/1/0/0.06 ^b		200, 0.87	2.9 × 10 ¹⁰	1.0 × 10 ⁻¹⁴
0.2/1/0/0.06 ^b		115, 0.87	5.2 × 10 ¹⁰	2.6 × 10 ⁻¹⁴

^a Calculated for 1% transmission through cloud layer, except on lines 1 and 4.

^b Corresponds to initial NH₃ abundance at room temperature, data from Table 4.

Electrical Discharges

Electric discharge is the last mechanism considered for organic synthesis in Titan's lower atmosphere. Toupance *et al.* (1974), have shown that electric discharges through $\text{CH}_4 - \text{N}_2$ mixtures in a flow system (26 mbar) produce mainly HCN, hydrocarbons, and a variety of saturated and unsaturated nitriles. Starting with a 90% N_2 /10% CH_4 mixture, about 60% of the CH_4 was converted to HCN. This conversion factor is used to estimate production of organic matter by electric discharges on Titan.

From the solar constant at Titan and an effective albedo of 0.2, the energy flux available is calculated to be $1.1 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}$. For lack of other relevant data, the conversion of this energy to electric discharges is assumed to proceed on Titan as it does on Earth with an efficiency of $10^{-3}\%$. Therefore, the energy flux carried as electric discharges would be $1.1 \times 10^{-8} \text{ J cm}^{-2} \text{ s}^{-1}$. Assuming a 5-km lightning stroke with a shock column of 80 cm^2 cross-section and a total energy of 10^{10} J (after Bar-Nun, 1975), a CH_4 number density of $5 \times 10^{18} \text{ cm}^{-3}$ in a 90% N_2 atmosphere, and a discharge energy flux of $1.1 \times 10^{-8} \text{ J cm}^{-2} \text{ s}^{-1}$, a production rate of $1.3 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$ or $6 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$ is obtained. This figure is appropriate for the lower atmosphere of the greenhouse models, and compares favorably with the production rates derived from hot H-atom reactions. However, the laboratory simulations of electric discharges on which the calculations are based may have little relevance to lightning discharges in a planetary atmosphere. Moreover, there is no clear information regarding the conversion efficiency of solar energy to electric discharge energy on any planet other than Earth. These considerations make statements about electric discharge synthesis of organic matter on Titan speculative. Interestingly, Bar-Nun (1975, 1978) suggests that the high $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ ratios observed on Jupiter may be manifestations of electric discharge phenomena.

V. SUMMARY

In recent years, several models have been proposed to account for available observations of Titan and to explain the processes that may be responsible. Although these models may differ in concept and function (e.g., greenhouse vs. inversion), several features must be common to all. Titan is undeniably red, which is most likely a result of the production of a colored organic layer on the surface or in the clouds.

Spectroscopic and polarimetric data indicate the existence of a layer of particles (photochemical haze) in the atmosphere, which may be thick enough to constitute clouds. Finally, in light of thermochemical equilibrium models, the presence of observable amounts of C_2H_6 , C_2H_2 and C_2H_4 indicate the occurrence of active organic chemical processes.

Nitrogen appears to be required in the atmosphere for the production of the uv-visible light absorbing dust in the stratosphere and of the reddish surface or clouds, or both. Although N_2 has not been observed in Titan's atmosphere, the probability of its existence is indicated by the inability of CH_4 and $CH_4 + H_2$ mixtures to yield colored products from particle bombardment or photochemistry. The presence of N_2 would require the existence of NH_3 in the atmosphere at some time in Titan's history and its subsequent photodissociation to produce the N_2 . Incorporation of nitrogen from NH_3 or N_2 or both into organic molecules by various processes would produce materials with the necessary spectroscopic properties.

In the upper Titan atmosphere where the gas densities are low, reactions initiated by particles (protons, electrons) may predominate, especially those coupling N_2 with CH_4 . It is not clear whether CH_4 can be coupled with N_2 photochemically ($\lambda > 1000 \text{ \AA}$), but this will be insignificant at best. Production rates of organic compounds of about $10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$ are estimated for processes initiated by solar winds, Saturn "wind," and cosmic rays. Cosmic-ray-induced reactions, however, will maximize much lower in the atmosphere than will the other particle-induced reactions. Hydrocarbons will be formed from particle reactions as well as from photochemical breakdown of CH_4 . Over 4.5×10^9 y spectroscopically observable materials (e.g., clouds or surface materials) should easily be produced.

Photochemical processes may predominate in the lower atmosphere below the clouds. Although the ultraviolet flux may be reduced by 2 - 4 orders of magnitude from the incident value, atmospheric photochemistry may nevertheless be significant from the occurrence of hot H atom reactions. The hot H atom may be produced from small amounts of NH_3 in the lower atmosphere. Production rates for organic matter are estimated to be about $10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ (Table 7), or ten times the upper-atmosphere rates. Electric discharges, if they occur, should produce about the same level of organic chemicals.

Thus, the surface of Titan should be covered by ancient or recent organic matter produced in the atmosphere. This material should include both hydrocarbons

and N-organics. Therefore, study of the satellite's surface in any lander mission should include organic analysis as a prime science objective, with particular attention to the chemistry of the organogenic elements H, C, N, O, and S.

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