

# Plasma Discharge in $N_2 + CH_4$ at Low Pressures: Experimental Results and Applications to Titan

W. REID THOMPSON, TODD J. HENRY,<sup>1</sup> JOEL M. SCHWARTZ,<sup>2</sup> B. N. KHARE, AND CARL SAGAN

*Laboratory for Planetary Studies, Space Sciences Building, Cornell University, Ithaca, New York 14853*

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## I. INTRODUCTION

We report the yields of gaseous hydrocarbons and nitriles produced in a continuous flow, low-dose, cold plasma discharge excited in a 10%  $CH_4$ , 90%  $N_2$  atmosphere at 295 K and pressures  $p$  of 17 and 0.24 mbar, and use the results to compute expected abundances of minor constituents in Titan's atmosphere. These experiments are, by design, relevant to the atmospheric chemistry induced by cosmic rays in Titan's troposphere and (at the lower pressure) to chemistry initiated by Saturnian magnetospheric electrons and other charged particle sources which excite stratospheric aurorae. At  $p = 17$  mbar, 59 gaseous species including 27 nitriles are detected in overall yield 4.0 (C + N) atoms incorporated into products per 100 eV (heV). At  $p = 0.24$  mbar, 19 species are detected, including six nitriles and three other unidentified N-bearing compounds; the yield is 0.79 (C + N)/heV, a mild decrease with pressure. The types of molecules formed change more markedly, with high degrees of multiple bonding at 0.24 mbar prevailing over more H-saturated molecules at 17 mbar. The molecules and yields at 0.24 mbar bear a striking resemblance to the minor constituents found in Titan's atmosphere, all of which are abundant products in the laboratory experiment. Using the altitude-integrated flux of charged particle energy deposition at Titan, the laboratory yields at  $p = 0.24$  mb, and a simple eddy mixing model, we compute absolute stratospheric column abundances and mole fractions. These are found to be in very good agreement with the Voyager IRIS observations. Except for the primarily photochemical products,  $C_2H_6$  and  $C_3H_8$ , the match is much better than that obtained by photochemical-kinetic models, demonstrating that properly designed laboratory experiments are directly applicable to modeling radiation-chemical processes in planetary atmospheres. On the basis of this agreement we expect  $CH_3-C\equiv N$  (ethanenitrile = acetonitrile),  $CH_2=CH-CH=CH_2$  (1,3-butadiene),  $CH_2=C=CH_2$  (1,2-propadiene = allene), and  $CH_2=CH-C\equiv CH$  (1-buten-3-yne) to be present at mol fractions  $X > 10^{-9}$ , and  $CH_2=CH-C\equiv N$  (propenenitrile),  $CH_3-CH=CH_2$  (propene), and  $CH_3-CH_2-C\equiv N$  (propanenitrile) at  $X > 10^{-10}$  in Titan's atmosphere. © 1991 Academic Press, Inc.

Prior to the Voyager flybys of November 1980 and August 1981, the atmosphere of Titan was known to contain  $CH_4$  (Kuiper 1944),  $C_2H_6$ , and  $C_2H_2$  (Gillett 1975, Low and Rieke 1974) and a probable infrared-inactive gaseous constituent (Trafton 1972, Lutz *et al.* 1976). Titan's reddish color and polarimetric evidence of a haze and/or cloud (Veverka 1974) led to the suggestion (Sagan 1974) that a UV-absorbing organic heteropolymer (Khare and Sagan 1973) produced in, and sedimenting through, the  $CH_4$ -containing atmosphere could explain Titan's optical properties. Hunten (1977), Atreya *et al.* (1978), and Chang *et al.* (1978) suggested the presence of  $N_2$ , derived from photolysis of  $NH_3$ , as an explanation for the infrared-inactive gaseous constituent. Using a simple thermal opacity model based on these constituents and a small amount of  $H_2$ , Hunten (1978) constructed a model of the atmosphere which was to prove remarkably similar, in many regards, to that found by Voyager.

Analysis of the Voyager IRIS data led to the detection of six simple hydrocarbons and three nitriles (organic molecules having the cyano,  $-C\equiv N$ , group) in the atmosphere of Titan (Hanel *et al.* 1981, Kunde *et al.* 1981, Maguire *et al.* 1981). These are formed by energetic chemical processes in the primarily  $N_2 + CH_4$  atmosphere (see Sagan and Thompson 1984, Hunten *et al.* 1984, Sagan *et al.* 1984). Titan's  $CH_4$  abundance varies from a nominal 8% at the surface to ~2% in the lower stratosphere (Lellouch *et al.* 1989, Thompson *et al.* 1990) and increases again to ~8% at high altitudes (Smith *et al.* 1982).

Prior to the Voyager encounter, a few experimenters had investigated the gas-phase and solid/liquid-phase products of photochemistry or (charged particle) radiation chemistry in  $N_2 + CH_4$  mixtures. (Here, we follow the standard terminology of the field by using the term *radiation* to mean ionizing radiation in the form of charged particles or photons with energies greater than typical chemical bond energies.) Most of this work was done in

<sup>1</sup> Now at Steward Observatory, University of Arizona, Tucson, AZ.

<sup>2</sup> Now at Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA.

the context of prebiotic chemistry on Earth, prompted by mounting evidence that  $N_2$  might be dominant over  $NH_3$  as the early repository of atmospheric nitrogen. Sanchez *et al.* (1966) had demonstrated the production of  $C_2H_6$ ,  $C_4H_2$  (butadiyne, or diacetylene),  $C_6H_6$  (benzene), HCN, and  $HC_2CN$  from high-frequency sparking of an  $N_2 + CH_4$  atmosphere with methane mol fraction  $X_{CH_4} = 0.25$  at pressure  $p = 1$  bar. Balestic (1974) studied MeV electron irradiation at  $X_{CH_4} = 0.50$  and  $p = 0.95$  bar, finding  $C_2H_6$ ,  $C_2H_4$ ,  $C_3H_8$ , HCN,  $CH_3CN$ , and  $CH_3CH_2CN$ . Scattergood *et al.* (1974, 1975) bombarded a mixture also having 50%  $CH_4$  at  $p = 0.79$  bar with 2 MeV protons, producing all six noncyclic  $C_2$  and  $C_3$  hydrocarbons, the three corresponding *iso*- $C_4$  compounds (2-methyl propane/ene/yne, also called isobutane/ene/yne),  $C_4H_2$ ,  $CH_3CN$  (but no HCN), and a reddish-brown liquid which contained unspecified alkanes and alkyl amines up to  $C_{22}$ . All of these investigations also studied  $CH_4 + NH_3$  mixtures, which were, in the past, much more frequently used in UV, charged particle, and electrical discharge experiments.

The Scattergood *et al.* experiments were conducted with outer planet applications in mind; the UV-VIS absorption properties of the red-brown liquid were suggested as relevant to Titan, and the possibility of an  $N_2$ -rich atmosphere of Titan was specifically addressed by Scattergood and Owen (1977), who compared Titan's spectrum with the UV-VIS and infrared spectra of the product from  $N_2-CH_4$  irradiation. Sagan (1974) had previously concluded that the reddish color of Titan was probably due to organic materials similar to those produced in some laboratory simulation experiments. However, all the above-mentioned experiments were conducted at  $CH_4$  abundances and pressures greater than those applicable to Titan, and furthermore, excepting Balestic (1974), quantitative analyses were not reported. In contrast, the extensive work of Toupance *et al.* (1974, 1975) on  $N_2-CH_4$  and  $NH_3-CH_4$  atmospheres provides quantitative information on the gaseous products produced in a 27 mbar, continuous-flow, 500 V DC coronal discharge at compositions varying from  $X_{CH_4} = 0$  to 1 in steps of 0.1, plus  $X_{CH_4} = 0.05$ . They identified several hydrocarbons and nitriles (up to  $C_4$ ) and percent yields which can be converted (with some uncertainty) to absolute yields.

A year before the Voyager 1 encounter, Chang *et al.* (1979) reviewed the expectations for organic chemistry on Titan. Chemical processes in both  $N_2-CH_4$  and  $NH_3-CH_4$  atmospheres were considered, since there was a fair a priori chance that Titan had a surface much warmer than its effective temperature of 84 K. ( $NH_3$  would be totally frozen out on the surface at 84 K; the Chang *et al.* working model had a 135 K surface.) While predictions about reddish organic solids, gaseous hydrocarbons, and hydrocarbon condensates would later be proven true (they even correctly predicted the order of the four most abundant

hydrocarbons), Chang *et al.* were led to discount both HCN and other nitriles as likely constituents of Titan's atmosphere. This can be attributed to the rather curious lack of HCN and most other nitriles (except  $CH_3CN$ ) in the Scattergood *et al.* experiments, the unavailability of Balestic's doctoral thesis, and the evidence that nitrogenous organics are not readily produced from UV irradiation of  $N_2-CH_4$  atmospheres. The Toupance *et al.* (1974) work was cited as an "electrical discharge" experiment, and was relegated to relevance only if lightning occurred on Titan, which was thought unlikely.

Actually, the coronal discharge in the Toupance *et al.* work involves no sparks, and, like the inductive plasma discharge in our experiments, is a process very similar to that which occurs along, and at the termini of, charged particle tracks (see Thompson *et al.* 1987). In these "cold plasma" processes, the electrons are highly superthermal, but the neutral molecules and ions remain near the ambient temperature. In contrast, a high voltage, high current arc, or a laser-induced breakdown, are hot plasmas, in which the kinetic and excitation temperatures of all species are very high. Cold plasmas are close analogs of electron and proton irradiation (and of aurorae), while hot plasmas are relevant to lightning discharges and meteoritic shocks and trails.

After the Voyager IRIS experiment revealed the hydrocarbons  $C_2H_6$ ,  $C_3H_8$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_3H_4$ , and  $C_4H_2$ , but also a substantial abundance of HCN and the nitriles  $NCCN$  and  $HC_2CN$ , the importance of radiation-induced nitrogen chemistry in Titan's atmosphere became apparent. Not long after, Gupta *et al.* (1981) qualitatively studied the gases resulting from a number of processes (UV, electric spark,  $\gamma$ -irradiation, 1.5-MeV protons, and 10-MeV electrons) acting on  $N_2 + CH_4$  atmospheres having 1.0–2.5%  $CH_4$ . The  $e^-$  bombardment was of condensed  $CH_4$  at 77 K overlain by 0.93 bar of  $N_2$ ; phase equilibria in this system indicate that the sample could have consisted of both liquid and solid  $CH_4-N_2$  mixtures overlain by a gas containing  $\leq 13\%$   $CH_4$  (see Thompson 1985, Thompson *et al.* 1990). Other experiments were performed at room temperature. The proton irradiation was carried out at 2 mbar pressure, and is the most relevant to Titan; six of the nine Voyager-observed molecules were produced, with HCN the most abundant product.

Raulin *et al.* (1982) reviewed the work of Toupance *et al.* (1975) and other workers in the context of the Voyager results, and presented new work (Bossard *et al.* 1983) demonstrating the effect of  $H_2$  on the  $N_2-CH_4$  system, and the effect of its removal on production rates in a closed system. Meanwhile, the importance of the solid products was reinvestigated with Titan specifically in mind: the optical constants of organic heteropolymer (tholin) produced from a DC discharge in a 10%  $CH_4$ ,  $N_2 + CH_4$  mixture at 0.2 mbar pressure (Khare *et al.* 1984a) proved, when used in light scattering models, to

be very compatible with Titan's reflection properties (Thompson 1984, Sagan *et al.* 1985, McKay *et al.* 1989).

Sagan and Thompson (1984) investigated another source of hazes: the condensation of organic gases in Titan's stratosphere. The gases detected by Voyager, as well as gases released by pyrolysis of a chemically related tholin (Khare *et al.* 1981), were considered candidates for the formation of (mostly colorless) condensate hazes below altitude  $z = 225$  km. Sagan and Thompson also investigated the contribution of chemical energy by the UV and charged particle sources at Titan, computing the altitude dependence of energy deposition rate. This work showed that solar wind and plasma protons and electrons at very high altitudes; magnetospheric electrons (energy  $E \leq 1$  MeV) at  $z \leq 300$  km, pressure  $p \leq 0.1$  mbar, in the stratosphere; and cosmic rays (energies to GeV–TeV) primarily at  $z = 100$ – $40$  km,  $p = 10$ – $150$  mbar in the troposphere, can all produce substantial amounts of organic gases and solids in Titan's atmosphere. It is evident from the Sagan and Thompson (1984) study that most of the radiation-induced chemistry takes place at pressures where no quantitative laboratory study of gas-phase chemistry has been performed.

Absolute reaction rate kinetic models offer another avenue to explaining or predicting the observed abundances in Titan's atmosphere. Because charged-particle-induced radiation chemistry is increasingly important at large heliocentric distances, purely photochemical models cannot hope to explain all aspects of energetic chemistry in outer planet/satellite atmospheres. For example, prior to the Voyager discoveries, no Titan photochemical models had included N<sub>2</sub> chemistry. The situation at Titan is especially sensitive to this omission: since only a small fraction of solar UV (wavelengths  $\lambda \leq 100$  nm, cf. Zahnle 1986) is capable of dissociating N<sub>2</sub>, most of the nitrogen chemistry originates with charged-particle dissociation of N<sub>2</sub>, which primarily produces atomic N. [This fact was realized by Capone *et al.* (1980, 1981), who predicted, pre-Voyager, the production of nitrogenous organics by cosmic rays in Titan's atmosphere.] The photochemical processes modified to include this radiolytic source of atomic N were reviewed by Strobel (1983), and an elaborate photochemical model including a simplified zero-dimensional atomic N input was published by Yung *et al.* (1984). The accuracy of such theoretical models depends on the completeness of the reaction network, and on the availability of reasonably accurate rate constants for each elementary chemical step. Examples of some potential pitfalls are seen in the update by Yung (1987) of nitrile production in the Yung *et al.* (1984) model. Yung (1987) points out that in the original model a critical rate was incorrect by a factor of  $2 \times 10^3$ , invalidating results for nearly all the nitrile species. Unfortunately, many of the important reaction rates are still not well known, and in any case, the multitude of reactions involved restricts (with the exception of homol-

ogous series) such models to molecules with no more than a few carbon + nitrogen atoms. For general products with  $(C + N) \geq 4$ – $6$ , predictions of abundance must currently derive from laboratory experiments (Sagan *et al.* 1984). In summary, (1) charged-particle chemistry must be included, and (2) laboratory simulations provide information independent of computational (photo-)chemical models, and can be important both in direct application to Titan and to identify uncertainties or important omissions in the computational models.

## II. EXPERIMENTAL METHODS

Most laboratory "simulation" experiments have, in the past, lacked both quantification and, in many cases, attention to environmental factors important if they are to be reliably applied to planetary environments. For a gas mixture irradiated in the laboratory, the most crucial environmental factors are pressure (which determines the ratio of uni-, bi-, and trimolecular processes) and dose per reactant molecule. In planetary stratospheres, the radiation chemistry occurs mainly at low pressures, and the rate of energy input is sufficiently low that, on characteristic mixing timescales, only a small fraction of the chemical bonds of the main atmospheric constituents is broken. Laboratory experiments should satisfy this low-dose constraint. The design of experiments should also ensure that the residence time of the gas in the reaction volume is sufficiently short that wall collisions are minimized or else should address the possibility of wall effects by varying the residence time (or reaction zone dimensions) or wall composition to assess their importance. Ambient temperature  $T$  is generally less important, unless key reactions rates are strongly temperature-dependent; nevertheless, temperature dependence should be studied where possible.

The execution of quantitative experiments at low dose, low pressure, and (often) low CH<sub>4</sub> abundance is a challenging laboratory task. A very low contaminant background, high throughput, and very sensitive analytical techniques must be employed. Reactive species must be isolated to minimize reactions prior to analysis. To meet this challenge and thereby extend laboratory measurements further in the direction of real planetary conditions, we have adopted and refined continuous-flow, inductive plasma discharge techniques, coupled with postirradiation gas chromatography/mass spectroscopy (GC/MS) for analysis of products.

We illustrate the basic layout in Fig. 1. A tank containing a gas of the desired composition supplies a steady flow of reactants at about 1 bar pressure; the flow rate is monitored by a digital flowmeter. The pressure drop to the  $10^{-1}$ – $10^2$  mbar working pressure occurs at the needle valve. The gas stream passes through a 77 K pretrap to

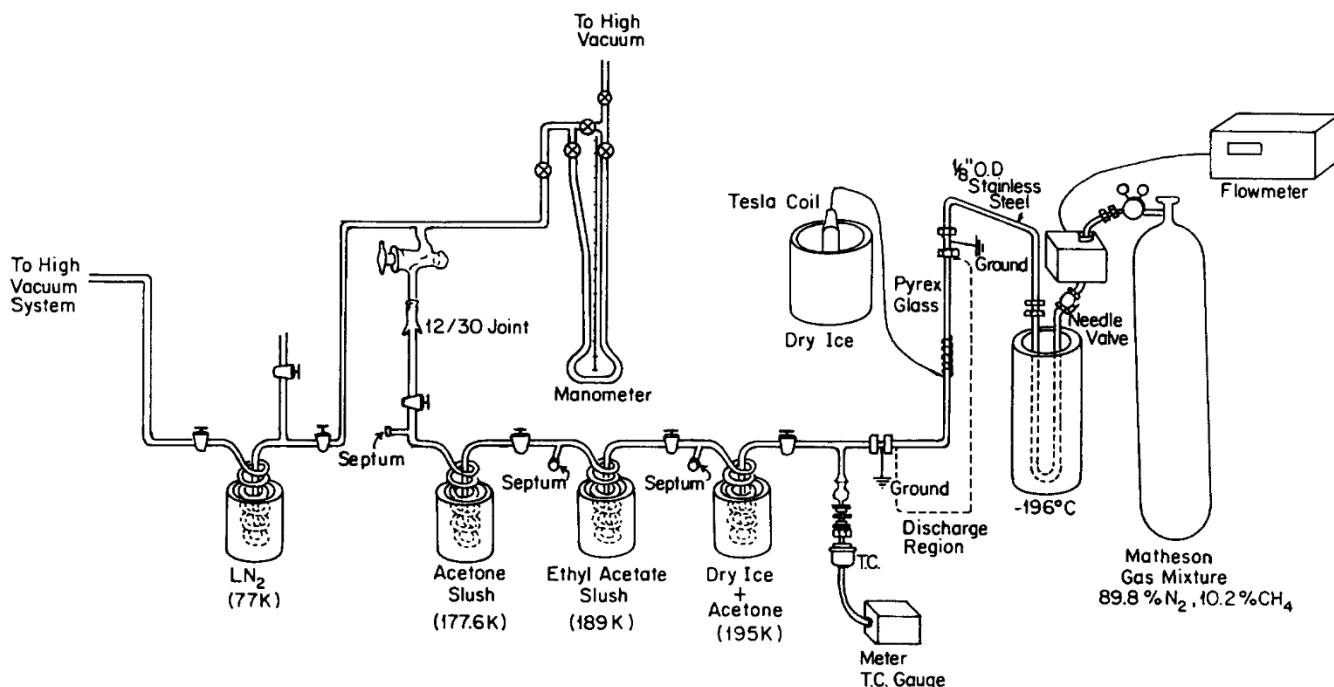


FIG. 1. Experimental layout for continuous flow plasma discharge irradiation experiments.  $\text{N}_2 + \text{CH}_4$  gas is introduced from the tank at right, the flow rate is measured, contaminant gases are removed by the pretrap, and an inductive discharge is excited by a Tesla coil or other radio frequency source as the gas flows through the glass discharge tube. Gas pressure is monitored by the T.C. (thermal conductivity) gauge. Products are fractionally trapped in four spirals of decreasing temperatures, and unreacted gas is pumped out continuously on left.

remove condensable, parts per million level contaminants, then flows through the reaction zone, typically traveling at a velocity of several  $\text{m sec}^{-1}$ . In the reaction zone, a plasma discharge is sustained by inductive coupling of a high-frequency generator (a cooled Tesla coil is sufficient) to the gas via a few turns of wire around the exterior. The plasma extends from the center of the glass tube to grounded stainless steel fittings at each end. A meter just downstream monitors the working pressure. The product gas rapidly flows through a series of cold traps; various temperatures are chosen (by trial and error) to separate the product molecules into nonreactive fractions. (Temperatures shown in Fig. 1 are near optimal for this  $\text{N}_2\text{-CH}_4$  system.) The noncondensable fraction of the gas then flows through a backflow-trap and out to the vacuum pumps. Stopcocks downstream of the traps were partially closed to achieve the desired steady-state pressure in the reaction/traps region.

By collecting product gases continuously, detectable quantities can be accumulated even though the amount of chemically active reactant flowing through the reaction zone is, at low pressures and/or  $\text{CH}_4$  abundances, very small. In the experiments described here, the dimension of the discharge region is about 7 mm I.D. by 150 cm length. The ratio of tube radius to gas mean free path at

the lowest pressure (0.24 mbar) is about 50; given the flow rate, only a small fraction of the molecules in the excited volume collides with the walls. Experiments of up to 100 hr duration were conducted. At the end of the run, contents of the traps were individually evaporated, the moles of gas determined manometrically and sampled for GC/MS analysis, sometimes recompressing in a manometer sidearm to increase the fraction injected. Samples were withdrawn in a gas-tight syringe of about  $10 \text{ cm}^3$  capacity and injected promptly into the GC/MS, a Hewlett-Packard 5880A GC/5970 MSD system with computerized data acquisition, analysis, and database search capabilities. A crosslinked methyl silicone "PONA" column, generally used for hydrocarbon analyses, was used. The GC was initially programmed to hold at an initial  $T = -20^\circ\text{C}$  for 15 min, then warmed at  $10^\circ\text{C min}^{-1}$  to a final temperature of  $250^\circ\text{C}$ . All detected molecules eluted within 80 min. In later runs, the initial  $T$  was further reduced to  $-60^\circ\text{C}$  to improve separation of the lightest ( $\text{C}_2$ ) products, which overlapped in most analyses, complicating quantification of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_6$  (in elution order).

Mass spectral database matches were confirmed by visual inspection. In several cases, the elution time was used to sort out isomers with very similar mass spectra. Many of the larger nitriles were not in the computer library



and were identified by manual analysis of the mass spectral fragmentation patterns. Quantification of the amounts injected into the GC/MS was achieved in a three-part process. Mixtures of hydrocarbon standards and of nitrile standards, both containing molecules representing the alkane, alkene, and alkyne classes, were injected into the GC/MS in calibration runs. The total ion count (TIC) of each component along with its known abundance in the injected standard yields its detection factor  $\beta = (\text{moles injected})/(\text{TIC})$ . In an experimental run, the  $\beta$  factors for molecules not present in the standard were estimated by homologous extrapolation of  $\beta$ 's from available standards with similar functional groups and/or geometric structure. While the relative  $\beta$ 's remained constant from day to day, the absolute sensitivity varied somewhat, but could be corrected by conservation of mass: the total moles detected in all products was summed and compared with the known moles of injected gas, providing a correction factor which was then applied uniformly to all computed quantities.

Determining quantitative yields further required a measurement of the total power delivered to the gas during the course of the experiment. This was calculated by using pure C<sub>2</sub>H<sub>4</sub>, flowed through the same system, as a calibration standard. The pressure dependence of the radiation yields  $G$  (in molecules per 100 eV or molec/heV) for the production of C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> from C<sub>2</sub>H<sub>4</sub>, down to  $p \approx 10$  mbar, are given by Sauer and Dorfman (1961). We used a best-fit, log-log extrapolation to estimate  $G$  values at lower pressures. The pressure dependence of the power delivered to the plasma was estimated by GC/MS analysis of the C<sub>2</sub>H<sub>2</sub> and CH<sub>4</sub> yields in six C<sub>2</sub>H<sub>4</sub> discharge experiments. The estimates of delivered power, 0.5 W at 17 mbar and 0.04 W at 0.24 mb, are uncertain by about a factor of two due to the uncertainty of the extrapolation and the variation in values computed from either the C<sub>2</sub>H<sub>2</sub> or the CH<sub>4</sub> yields (with C<sub>2</sub>H<sub>2</sub>-derived values systematically higher). While the *relative* accuracy between yields for molecules produced at a given pressure is much higher, this absolute uncertainty carries through to the results presented in the following sections. (This error is at most comparable to, and in most cases much less than, the uncertainties in the Voyager IRIS measurements.)

Two experiments on plasma chemistry in N<sub>2</sub> + CH<sub>4</sub> with  $X_{\text{CH}_4} = 0.102$  are reported here; one at 17 mb, the other at 0.24 mb. Results for a similar experiment at  $X_{\text{CH}_4} = 10^{-3}$  are reported by Thompson *et al.* (1989). Five experiments and a series of trapping tests run prior to those reported provided initial results and guided improvements of the technique and adjustment of the trap temperatures. The most important modifications of early designs were (1) removing all plastics from the region near the discharge and (2) adding a pretrap to capture

<i>Pressure:</i>	17 mbar	0.24 mbar
<i>Experiment Time:</i>	49 <sup>h</sup> 34 <sup>m</sup>	49 <sup>h</sup> 17 <sup>m</sup>
<i>Gas Flowed:</i>	3.150 mol 5.979 mol (C+N) (4100ℓ)	0.0531 mol 0.1008 mol (C+N) (4900ℓ)
<i>Energy Delivered:</i>	$5.6 \times 10^{23}$ eV	$4.4 \times 10^{22}$ eV
<i>Overall (C+N) in Products:</i>	0.62 atom-%	0.58 atom-%
<i>G<sub>tot</sub>, Product (C+N)/100eV</i>	4.0	0.79

FIG. 2. Experiment profiles and overall yields for the continuous flow plasma discharge irradiation experiments reported here. The total production efficiency  $G_{\text{tot}} = \sum_i (n_C + n_N)_i G_i$  where  $i$  ranges over all detected molecules,  $(n_C + n_N)_i$  is the sum of the number of C and N atoms in a given molecule, and  $G_i$  is the production efficiency for a given molecule.  $G_{\text{tot}}$  for the 17 mbar experiment includes rough estimates of the C<sub>2</sub> hydrocarbons;  $G_{\text{tot}}$  exclusive of the C<sub>2</sub> hydrocarbons is 2.1.

condensable contaminants in the reactant gas. The experimental parameters and yields summed over all gaseous products are given in Fig. 2. Both experiments ran about 50 hr, and were monitored continuously to refill traps and adjust the flow rate and reaction zone pressure, which varied ~5% about the mean values listed. Volumes listed are true (not STP) volumes.

Two types of control experiments—continuous flow plasma discharge in pure N<sub>2</sub>, and continuous flow without discharge in the N<sub>2</sub> + CH<sub>4</sub> mixture—were performed. Only negligibly small levels of contaminants were found: these controls proved all the molecules reported below to be true products of the N<sub>2</sub> + CH<sub>4</sub> plasma chemistry.

### III. EXPERIMENTAL RESULTS

From Fig. 2 we see that the dose applied to the flowing gas constituted at most 1.4 eV molec<sup>-1</sup>. Since about 30 eV is required to produce an ion pair in N<sub>2</sub> or CH<sub>4</sub>, a maximum of 5% of the reactant molecules was ionized, so that, as desired, the results represent initial rates and not a local radiation-chemical equilibrium (or some point along an evolution toward such an equilibrium) which would result if the dose constituted the ionization of every reactant molecule many times over. About 0.6 atom-% of the reactant gas was converted to gaseous products captured in the traps. (Only H<sub>2</sub> and the reactant gases N<sub>2</sub> and CH<sub>4</sub> are volatile enough to avoid trapping by the 77 K trap.) Brown to reddish-brown solids were also pro-

TABLE I  
Product Yields for Continuous Flow Plasma Discharge  
Irradiation of 90% N<sub>2</sub>, 10% CH<sub>4</sub> at 17 mbar Pressure

Molecule	Yield, molec/heV <sup>a</sup>
ethyne	ND <sup>b</sup>
propane	3.98 × 10 <sup>-1</sup>
ethane	ND <sup>b</sup>
methanenitrile	1.64 × 10 <sup>-1</sup>
ethene	ND <sup>b</sup>
propene	5.48 × 10 <sup>-2</sup>
methylpropane	2.29 × 10 <sup>-2</sup>
propyne	1.91 × 10 <sup>-2</sup>
butane	1.90 × 10 <sup>-2</sup>
propadiene	1.65 × 10 <sup>-2</sup>
propynenitrile	8.80 × 10 <sup>-3</sup>
ethanenitrile	4.57 × 10 <sup>-3</sup>
cis-2-butene	3.57 × 10 <sup>-3</sup>
2-methylbutane	3.20 × 10 <sup>-3</sup>
propanenitrile	3.17 × 10 <sup>-3</sup>
ethanedinitrile	2.82 × 10 <sup>-3</sup>
trans-2-butene	2.57 × 10 <sup>-3</sup>
1-butene	2.33 × 10 <sup>-3</sup>
2-methylpropene	2.04 × 10 <sup>-3</sup>
1-buten-3-yne	1.73 × 10 <sup>-3</sup>
1,3-butadiene	1.73 × 10 <sup>-3</sup>
2-butyne	1.58 × 10 <sup>-3</sup>
1,3-butadiyne	1.54 × 10 <sup>-3</sup>
pentane	1.42 × 10 <sup>-3</sup>
2-propenenitrile	1.34 × 10 <sup>-3</sup>
cyclopropane	9.3 × 10 <sup>-4</sup>
2,2-dimethylpropane	7.8 × 10 <sup>-4</sup>
1,2-butadiene	6.0 × 10 <sup>-4</sup>
2-methylpropanenitrile	4.7 × 10 <sup>-4</sup>
1-butyne	4.4 × 10 <sup>-4</sup>
cis-2-pentene	3.1 × 10 <sup>-4</sup>
2,2-dimethylbutane	3.0 × 10 <sup>-4</sup>
cyclobutane	2.9 × 10 <sup>-4</sup>
2-methyl-2-butene	2.8 × 10 <sup>-4</sup>
2-methylpentane	2.8 × 10 <sup>-4</sup>
2-methyl-1-butene	2.4 × 10 <sup>-4</sup>
2,2-dimethylpropanenitrile	2.4 × 10 <sup>-4</sup>
butanenitrile	2.0 × 10 <sup>-4</sup>
1-pentene	1.4 × 10 <sup>-4</sup>
trans-2-pentene	1.4 × 10 <sup>-4</sup>
3-methyl-1-butene	1.3 × 10 <sup>-4</sup>
cis-2-butenenitrile	1.0 × 10 <sup>-4</sup>
2-butyne	9 × 10 <sup>-5</sup>
trans-2-butenenitrile	6 × 10 <sup>-5</sup>
3-butenenitrile	5 × 10 <sup>-5</sup>
3-methyl-3-butenenitrile	4 × 10 <sup>-5</sup>
1,3-cyclopentadiene ?	3 × 10 <sup>-5</sup>
2-methyl-2-propenenitrile	3 × 10 <sup>-5</sup>
cis,trans-2-methyl-2-butenenitrile	2 × 10 <sup>-5</sup>
trans-3-pentenitrile	1.2 × 10 <sup>-5</sup>
2,4-hexadienenitrile ?	1.0 × 10 <sup>-5</sup>
2,4-pentadienenitrile	8 × 10 <sup>-6</sup>
2-methylene-3-butenenitrile	5 × 10 <sup>-6</sup>
3-diazo (propyne or butadiene) ??	5 × 10 <sup>-6</sup>
cis-2-pentenitrile	5 × 10 <sup>-6</sup>
1,2,4,5-tetraazine	4 × 10 <sup>-6</sup>
trans-2-pentenitrile	4 × 10 <sup>-6</sup>

TABLE I—Continued

Molecule	Yield, molec/heV <sup>a</sup>
2-methyl-3-butenenitrile	3 × 10 <sup>-6</sup>
4-pentenitrile	3 × 10 <sup>-6</sup>
?,?-dimethylbutanedinitrile	2 × 10 <sup>-6</sup>
?-methylpentanenitrile	2 × 10 <sup>-6</sup>
?-methylpentanedinitrile	1 × 10 <sup>-6</sup>

<sup>a</sup> 1 molec/heV = 10.4 nmole J<sup>-1</sup> = 6.25 × 10<sup>8</sup> molec erg<sup>-1</sup>.

<sup>b</sup> ND, not determined because of experimental difficulties. For completeness, C<sub>2</sub> hydrocarbon yields can be roughly estimated as: C<sub>2</sub>H<sub>2</sub>: ~5 × 10<sup>-1</sup>; C<sub>2</sub>H<sub>4</sub>: ~3 × 10<sup>-1</sup>; C<sub>2</sub>H<sub>6</sub>: ~1 × 10<sup>-1</sup> (based on our early experiments at 6 mbar and results of Drost *et al.* (1976) and Scattergood *et al.* (1989) near 1 bar).

duced on the tube walls in both experiments; these tholins are similar in appearance to those studied by Khare *et al.* (1984a). The yield of solids was not determined. For gases, the yield computed in terms of total atoms of C and N summed over all product molecules per unit energy,  $G_{\text{tot}}$ , decreases by only about a factor of 5 despite a factor of 70 drop in pressure; the fact that there is some drop probably reflects the decrease of three-body collisions as  $p$  decreases.

The molecules detected as gaseous products at 17 mbar and at 0.24 mb, and their yields computed as described above, are shown in Tables I and II. (Separate samplings, GC/MS injections, and analyses were made for each of the four traps. Species found in more than one trap were summed to produce the yields shown in Tables I and II.) We emphasize that these constitute only a specific fraction of all molecules produced: those which are volatile enough to evaporate from the traps and stable enough to survive 10–30 min at room temperature and thereby form a part of the gas sample which was injected. Despite the multiple traps, reactive gaseous species such as isocyanides and azides may react to form other gaseous and/or condensed products. Many less volatile species remained as a film of solid and/or adsorbed liquid in the traps or on the reaction zone walls. These additional products have not yet been analyzed.

A great number of products are found in the 17-mbar experiment, which is relevant to pressures in Titan's atmosphere where most of the cosmic ray energy is deposited (i.e.,  $p = 150$  to 10 mb,  $z = 40$  to 100 km; see Fig. 3 of Sagan and Thompson 1984, hereinafter referred to as Paper I.) At 17 mb, 59 molecules are found, including 27 nitriles and two other N-bearing compounds. Aside from hydrocarbons, nitriles completely dominate: no amines were found down to the practical detection limit of  $G \approx 10^{-6}$  molec/heV, which corresponds to a mol fraction of  $10^{-6}$ – $10^{-7}$  in the product. (1 heV  $\equiv$  1 hectoeV  $\equiv$  100 eV = 6.25 × 10<sup>8</sup> molec erg<sup>-1</sup> = 10.4 nmol J<sup>-1</sup>.) Amines were

TABLE II  
Product Yields for Continuous Flow Plasma Discharge  
Irradiation of 90% N<sub>2</sub>, 10% CH<sub>4</sub> at 0.24 mbar Pressure

Molecule	Yield, molec/heV <sup>a</sup>
ethyne	$1.58 \times 10^{-1}$
ethene <sup>b</sup>	$9.01 \times 10^{-2}$
ethane <sup>b</sup>	$8.06 \times 10^{-2}$
methanenitrile	$3.26 \times 10^{-2}$
propane <sup>b</sup>	$1.17 \times 10^{-2}$
ethanedinitrile	$3.57 \times 10^{-3}$
propynenitrile	$2.44 \times 10^{-3}$
ethanenitrile	$1.46 \times 10^{-3}$
propyne	$1.36 \times 10^{-3}$
1,3-butadiene	$1.34 \times 10^{-3}$
1,3-butadiyne	$8.2 \times 10^{-4}$
propadiene	$7.7 \times 10^{-4}$
1-buten-3-yne	$2.4 \times 10^{-4}$
propenenitrile	$1.9 \times 10^{-4}$
propene	$9.3 \times 10^{-5}$
C <sub>3</sub> H <sub>3</sub> N ?	$5 \times 10^{-5}$
propanenitrile	$4 \times 10^{-5}$
1- <i>H</i> -tetraazole ?	$3 \times 10^{-5}$
CH <sub>3</sub> N <sub>3</sub> ?	$3 \times 10^{-6}$

<sup>a</sup> 1 molec/heV = 10.4 nmole J<sup>-1</sup> = 6.25 × 10<sup>8</sup> molec erg<sup>-1</sup>.

<sup>b</sup> Determined from separate 0.24 mbar experiment.

not found from N<sub>2</sub> + CH<sub>4</sub> by Balestic (1974), but were reported by Scattergood *et al.* (1975). They were not detectable by the techniques employed by Toupance *et al.* (1975) or Gupta *et al.* (1981). Because of the tendency for strong adsorption and peak spreading on most GC columns, the detectability of amines in our analysis is not ideal, so this question should be reinvestigated in further experiments. Note also that the C<sub>2</sub> hydrocarbons are not listed here because they were either lost from possible premature warming of the 77 K trap, or obscured by the air peak on the GC elution. Estimates based on other experiments (see Table I caption) were used in order to compute  $G_{\text{tot}}$  in Fig. 2.

The products include hydrocarbons with single, double, and triple bonds, with homologous members often present in roughly equal yields (within a factor of 10). The same is true for nitriles: taking the C<sub>2</sub>H<sub>x</sub>CN series as an example, we see yields  $G = 0.0088$ ,  $0.0032$ , and  $0.0013$  molec/heV, respectively, for propyne-, propane-, and propenenitrile. Methyl and dimethyl substitution is very common, and two (possibly four) ring compounds are also found. While nitriles are common, hydrocarbons are generally more abundant, forming six of the seven molecules with yields above  $G = 10^{-2}$  molec/heV. Many conjugated (alternating) multiple bonds, especially diene/ynes and 2-alkene/yne nitriles, are found, as expected on the grounds both of increased stability and of likely mechanisms of formation.

The situation for  $p = 0.24$  mbar (Table II) is dramatically different. Although a very small amount of product was formed (about 4.1 mg), the injection of a large fraction of the total product partially compensated, resulting in a minimum detectable  $G$  of about  $10^{-5}$  molec/heV. Nineteen gases are found (compared with 48 with  $G > 10^{-5}$  molec/heV at 17 mb), and the type of abundant molecules found has radically changed. With the exception of C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>, compounds with high orders of multiple bonding almost totally dominate the product list. At least six of the molecules ( $\geq 32\%$ ) have conjugated multiple bonds, and branched-chain hydrocarbons or nitriles are totally absent from the list. The 11 most abundant compounds include all 9 detected by Voyager—an observation immediately suggesting that charged particle precipitation at stratospheric altitudes is qualitatively sufficient to explain the detected organic gases on Titan.

We further investigate the differences between the 17 and 0.24 mbar experiments in two ways. In Fig. 3 we show the change of abundance for the 13 compounds common (both resolved and positively identified) to both experiments. In Figs. 4 and 5 we plot “abundance-complexity profiles,” plots of  $\log G$  versus the (C + N) sum for a given molecular class. The slopes on these plots give some idea of the rapidity with which the yields of different molecules in the product mixture decrease with increasing molecular mass, and allow in a gross sense extrapolation of abundances to higher (C + N) number. (The abundance of a specific compound cannot be predicted, but the probable overall abundance of compounds with a given bonding type can be estimated.) The mean slope is steeper at 0.24 mbar ( $\sim -0.85$ ) than at 17 mbar ( $\sim -1.05$ ). While the slope at 17 mbar is independent of the degree of multiple bonding, at 0.24 mbar the slope is generally much gentler for molecules with multiple and conjugated bonds than for saturated species, which show slopes as steep as  $-2.0$ . We return to these slopes, in the Titan context, below.

Most previous experiments have not had the combination of sensitivity, quantification, and attention to minor products to allow detailed comparisons with our results, but for several different types of radiation, plasma, and spark studies we can compare the HCN and sometimes C<sub>2</sub>H<sub>2</sub> yields (Table III).  $G_{\text{HCN}}$  is around 0.6–0.9 molec/heV near 1 bar, but shows a clear pressure dependence, decreasing to 0.10–0.16 molec/heV for  $p = 15$ –30 mb. Considering the experimental demands of quantitative work and the different energy sources, absolute agreement to the degree indicated in Table III is remarkable. The effect of varying  $X_{\text{CH}_4}$  is not evident here, but was investigated in detail by Toupance *et al.* (1975), who systematically varied  $X_{\text{CH}_4}$  from 0 to 1 by increments of 0.1, plus  $X_{\text{CH}_4} = 0.05$ , for both N<sub>2</sub> + CH<sub>4</sub> and NH<sub>3</sub> + CH<sub>4</sub> mixtures. The variation of HCN yield from N<sub>2</sub> + CH<sub>4</sub>

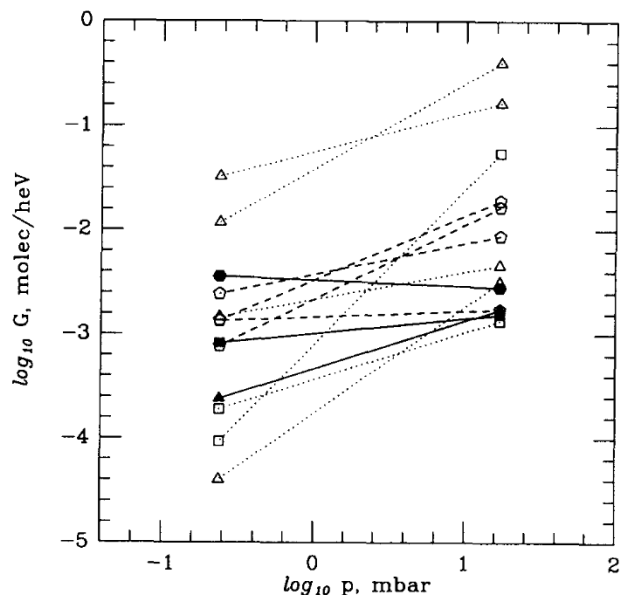


FIG. 3. Change in the production efficiencies  $G$  (molec/heV) for the thirteen species detected both in the 17 mbar and the 0.24 mbar experiments. The symbols here and in Figs. 4 and 5 code the multiple bond number, defined as  $m = n_{\text{double}} + 2n_{\text{triple}}$ , aside from the  $\text{—C}\equiv\text{N}$  triple bond of nitriles. Open triangles:  $m = 0$ ; open squares:  $m = 1$ ; open pentagons:  $m = 2$ ; filled triangles:  $m = 3$ ; filled squares:  $m = 4$ ; filled pentagons: rings; filled hexagons: dinitriles and non-nitrile, N-containing species. Dotted lines connect  $m = 0, 1$  species; dashed lines,  $m = 2$ ; and solid lines,  $m \geq 3$ —illustrating the tendency for more saturated (low  $m$ ) species to drop rapidly in yield as  $p$  decreases, while multiple bonded (high  $m$ ) species remain abundant.

between  $X_{\text{CH}_4} = 0.05$  and (maximum HCN at)  $X_{\text{CH}_4} = 0.30$  is about a factor of 3.

The one study from which quantitative information for many hydrocarbons and nitriles can be derived (however, with a small unknown multiplicative correction) is also that of Toupance *et al.* (1975). In their experiments a DC coronal discharge was applied to a gas flowing through a 10-cm-long cylindrical brass anode, 2.0 cm in diameter, with a central axial wire cathode 0.1 cm in diameter. The reaction volume is then  $31.34 \text{ cm}^3$ . Assuming an ambient  $T \approx 21^\circ\text{C}$  and with a reported residence time of 3 sec within the anode, current of 100 mA, and voltage 500 V, the dose can be computed to be 45.5 eV per molecule of reactant gas. (This experiment therefore moderately violates the low-dose criterion mentioned above.) Total analysis of the product gas was reported as a percentage of each species (including  $\text{H}_2$  and unreacted  $\text{N}_2$  and  $\text{CH}_4$ ), but the sum of these gaseous species leaves out the solids which must have been deposited on the inside of the tube. Here we compute yields  $G$  from the Toupance *et al.* data with the assumption that all of the reactant mass was recovered in product gases. A fraction  $f$  of the initial

mass in solid products would require multiplication of the computed values by the fraction  $(1 - f)$ .

We compare our yields at 17 mbar with those of Toupance *et al.* at 27 mbar in Table IV. For HCN, NCCN,  $\text{CH}_3\text{CN}$ , and  $\text{CH}_3\text{CH}_2\text{CN}$  the yields are similar, while the Toupance *et al.* yields for propene- and propynenitrile are about 0.1 of ours. For hydrocarbons, it is evident that

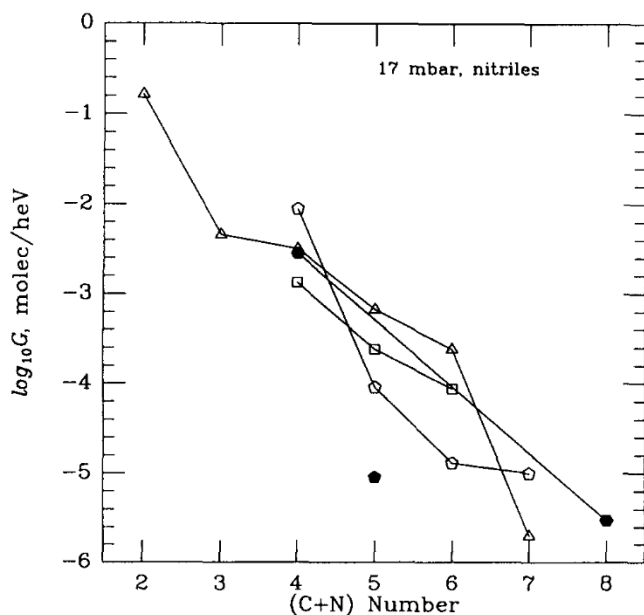
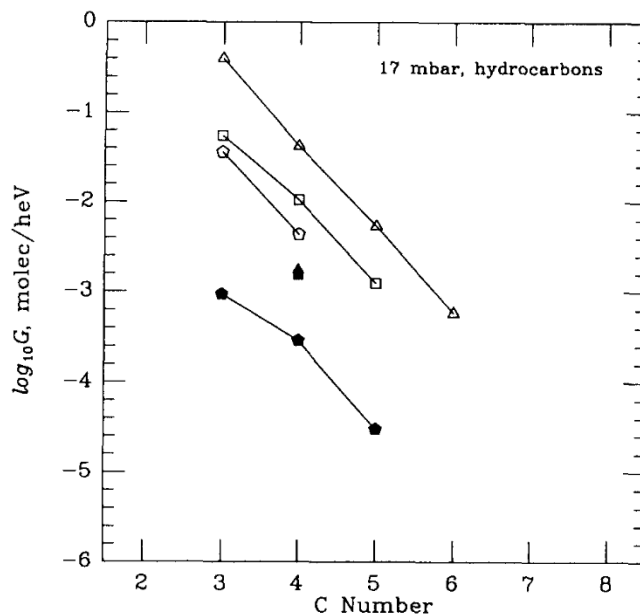


FIG. 4. Abundance-complexity profiles for hydrocarbons and nitriles in the 17 mbar experiment. See Fig. 3 caption for symbol codes. The average slope is about  $-0.9$  for hydrocarbons and about  $-0.8$  for nitriles. There is no significant dependence of slope on degree of multiple bonding at this pressure.

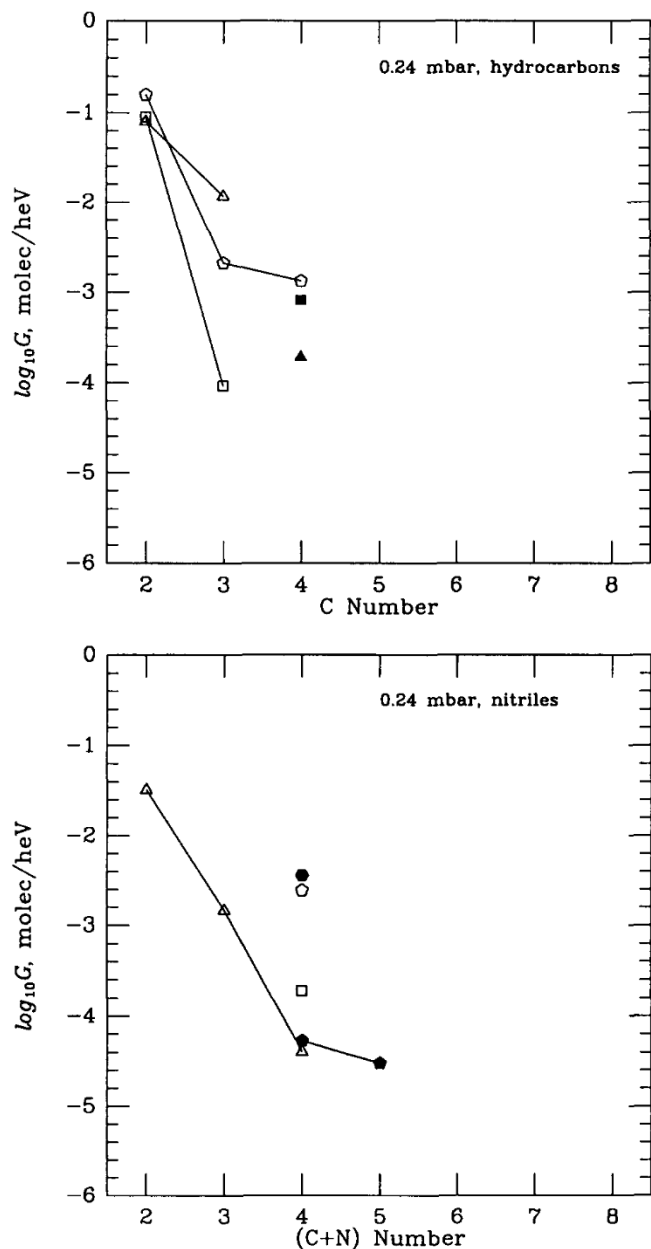


FIG. 5. Abundance-complexity profiles for hydrocarbons and nitriles in the 0.24 mbar experiment. See Fig. 3 caption for symbol codes. The average slope is about  $-1.1$  for hydrocarbons and about  $-1.0$  for nitriles, but species with less multiple bonding (open triangles and squares) generally decrease in abundance more rapidly with molecular mass, having slopes as steep as  $-1.5$  to  $-2.0$ .

the yields in our experiment are much higher, by factors around 10–1000. This difference for hydrocarbons may be due to the difference in doses:  $45.5 \text{ eV molec}^{-1}$  versus  $1.4 \text{ eV molec}^{-1}$  in our work. The high dose may convert most of the hydrocarbons to nitriles and/or to relatively involatile molecules, effectively removing hydrocarbons from the Toupance *et al.* gas phase sample.

Our low-radiation-dose results are analogous to production along isolated particle tracks in planetary atmospheres. They also bear some similarities to the “initial rates” reported by Bossard *et al.* (1983) for the formation of several hydrocarbons and nitriles in N<sub>2</sub> + CH<sub>4</sub> atmospheres in a closed system (and without or with H<sub>2</sub> escape). The lack of energy calibration in the Bossard *et al.* work prevents a quantitative comparison with the other results shown here.

#### IV. TITAN APPLICATIONS

In this section we utilize the laboratory results to assess and update the estimates made in Sagan and Thompson (1984, Paper I), and then proceed to use a simple atmospheric mixing model, along with previously computed charged particle energy input rates for Titan, to make quantitative predictions of the abundances of hydrocarbons and nitriles in the atmosphere, finally comparing the results with IRIS-derived abundances and with photochemical models.

First we consider some overall trends. The overall  $G$  values in Fig. 2 correspond to  $25 \text{ eV}/(C + N)$  at 17 mbar and  $126 \text{ eV}/(C + N)$  at 0.24 mbar (energy required per C or N atom incorporated into product). Scattergood (quoted in Chang *et al.* 1979) found about  $44 \text{ eV}/C$  in his proton irradiation of 1:1 N<sub>2</sub> + CH<sub>4</sub> at 800 mb, or  $22 \text{ eV}/(C + N)$  ( $G = 4.6$ ) if we assume C:N  $\approx$  1 in his product. This is comparable to our 17 mbar result and to the energy required to produce an ion pair, about 32 eV. In Paper I we adopted 32 eV as the quantity of energy required per (C or N) incorporated into products; this is equivalent to  $G_{\text{tot}} = 3.2 (C + N)/\text{heV}$ , while at 17 mbar we find  $4.0 (C + N)/\text{heV}$ . The Paper I estimate is reasonable for 10–1000 mbar pressures, but our 0.24 mbar result,  $G_{\text{tot}} = 0.79 (C + N)/\text{heV}$ , shows that it probably overestimates the low-pressure yield. However, we do not know this with certainty until the yield of solids can be determined in future experiments.

The mean slope in Fig. 4 (17 mb) is about  $-0.85$ , while in Fig. 5 (0.24 mb) it is about  $-1.05$ . A slope of  $-1$  corresponds to the  $\alpha = 1$  case of Paper I. (The values  $\alpha$  there are the magnitudes of the slopes.) The interplay of such an abundance profile with the characteristic dependence of vapor pressure on molecular mass was investigated in Paper I, for slopes of 0 to  $-1$ . The general trend (Paper I, Fig. 8) for a slope of  $-1$  indicates that most or all of the hydrocarbons and nitriles (and relatively nonpolar compounds in general) formed on Titan should condense in the main cloud, near and below 2800 km radius ( $z = 225 \text{ km}$ ). However, this *does not* rule out the possibility that particularly abundant compound(s) may form the Voyager-observed detached haze; future quantitative

TABLE III  
Comparison of HCN and C<sub>2</sub>H<sub>2</sub> Radiation Yields

Energy source	Pressure (mbar)	X <sub>CH<sub>4</sub></sub>	G <sub>HCN</sub> (molec/heV)	G <sub>C<sub>2</sub>H<sub>2</sub></sub> (molec/heV)	Reference
Reactor radiation	1013	0.06	0.90		Zhdamirov <i>et al.</i> (1971)
		0.30	0.20		
Laser shock plasma	~1013	0.03	0.90	0.48	Scattergood <i>et al.</i> (1989)
		0.10	2.4	1.9	
Spark (3 kV arc)	933	0.14	0.56	0.30	Drost <i>et al.</i> (1976)
Spark (20 kV arc)	~1013	0.03	0.45	0.12	Scattergood <i>et al.</i> (1989)
		0.10	0.75	0.48	
Spark (RF)	267	0.50	0.26		Stribling and Miller (1987)
Coronal discharge (DC)	27	0.05	0.072	0.002	Toupance <i>et al.</i> (1975)
		0.10	0.12	0.005	
		0.25	0.19	0.018	
		0.30	0.20	0.023	
Plasma discharge	13-27	0.25	0.095		Capezzuto <i>et al.</i> (1973)
		0.10	0.16		
Plasma discharge	17	0.10	0.16		This work
	0.24	0.10	0.033	0.16	

analysis of the products formed in our experiments which were too involatile for gas-phase injection (both residual trap contents and tholin components) may shed some light on this possibility.

Provided relevant pressures and compositions are investigated, low-dose, continuous-flow, quantitative

plasma irradiation experiments such as those presented here should be directly applicable to computing primary production rates for molecules on Titan. Some complication arises because no constant abundance X<sub>CH<sub>4</sub></sub> applies to the entire Titanian stratosphere; X<sub>CH<sub>4</sub></sub> above the stratospheric temperature minimum (at z ≈ 42 km) is 0.020 (Thompson *et al.* 1990), while the value rises above the homopause (at z ≈ 750 km) to 0.08 at 1100 km (Smith *et al.* 1982). While the comparisons below indicate that our results for X<sub>CH<sub>4</sub></sub> = 0.102 are relevant to the (average) Titan stratospheric environment, it would be interesting to perform similar experiments at X<sub>CH<sub>4</sub></sub> = 0.020. [Also, while we do not present detailed comparisons here, our results for p = 0.56 mbar, X<sub>CH<sub>4</sub></sub> = 10<sup>-3</sup> (Thompson *et al.* 1989) indicate that yields do not decrease drastically with decreasing X<sub>CH<sub>4</sub></sub>.]

A main goal of our work was to achieve the quantitative detection limits (corresponding to collection and analysis of microgram quantities of gases) necessary to perform an experiment at pressures approaching those appropriate to real Titanian auroral chemistry. Saturnian magnetospheric electrons are abundant up to energies of about 1 MeV, and their energy deposition zone extends through several hundred kilometers of altitude, as deep as the 0.1-mbar level (Paper I, Fig. 3). Our 0.24-mbar experiment is therefore relevant, at least, to radiation-chemical processing near the lowest part of this zone, while the 17-mbar experiment is applicable to cosmic ray processes in Titan's troposphere. While we hope that future experiments using these techniques will match the Titanian environment even better, we proceed to use the 0.24 mbar results to compute the expected abundances of the experimental products in Titan's atmosphere.

TABLE IV  
Comparison of Hydrocarbon and Nitrile Yields near 20 mbar Pressure

Molecule	G, molec/heV (this work)	G, molec/heV (Toupance <i>et al.</i> 1975)
H-C≡N	1.6 × 10 <sup>-1</sup>	1.2 × 10 <sup>-1</sup>
HC≡CH	—	3.9 × 10 <sup>-3</sup>
CH <sub>3</sub> -CH <sub>3</sub>	—	2.8 × 10 <sup>-3</sup>
CH <sub>2</sub> =CH <sub>2</sub>	—	4.6 × 10 <sup>-4</sup>
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	4.0 × 10 <sup>-1</sup>	—
CH <sub>3</sub> -CH=CH <sub>2</sub>	5.5 × 10 <sup>-2</sup>	—
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>3</sub>	2.3 × 10 <sup>-2</sup>	7.2 × 10 <sup>-5</sup>
CH <sub>3</sub> -C≡CH	1.9 × 10 <sup>-2</sup>	1.0 × 10 <sup>-4</sup>
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	1.9 × 10 <sup>-2</sup>	[2.3 × 10 <sup>-5</sup> ]
<i>trans</i> -CH <sub>3</sub> -CH=CH-CH <sub>3</sub>	2.6 × 10 <sup>-3</sup>	—
CH <sub>2</sub> =C=CH <sub>2</sub>	1.6 × 10 <sup>-2</sup>	—
NH <sub>3</sub>	—	6.6 × 10 <sup>-3</sup>
N≡C-C≡N	2.8 × 10 <sup>-3</sup>	5.7 × 10 <sup>-3</sup>
CH <sub>3</sub> -C≡N	4.6 × 10 <sup>-3</sup>	4.2 × 10 <sup>-3</sup>
<i>cis</i> -CH <sub>3</sub> -CH=CH-CH <sub>3</sub>	3.6 × 10 <sup>-3</sup>	—
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -CH <sub>3</sub>	3.2 × 10 <sup>-3</sup>	—
CH <sub>3</sub> -CH-CH <sub>2</sub> -CH <sub>3</sub>	2.3 × 10 <sup>-3</sup>	—
CH <sub>3</sub> -C(CH <sub>3</sub> )=CH <sub>2</sub>	2.0 × 10 <sup>-3</sup>	[7.0 × 10 <sup>-5</sup> ]
CH <sub>3</sub> -CH-CH=CH <sub>2</sub>	1.7 × 10 <sup>-3</sup>	—
CH <sub>2</sub> =CH-C≡CH	1.7 × 10 <sup>-3</sup>	—
CH <sub>2</sub> -C≡C-CH <sub>3</sub>	1.6 × 10 <sup>-3</sup>	—
HC≡C-C≡CH	1.5 × 10 <sup>-3</sup>	—
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	1.4 × 10 <sup>-3</sup>	—
CH <sub>3</sub> -CH <sub>2</sub> -C≡N	3.2 × 10 <sup>-3</sup>	1.3 × 10 <sup>-5</sup>
HC≡C-C≡N	8.8 × 10 <sup>-3</sup>	4.4 × 10 <sup>-4</sup>
CH <sub>2</sub> =CH-C≡N	1.3 × 10 <sup>-3</sup>	3.7 × 10 <sup>-4</sup>



For molecules which are not significantly destroyed by other processes subsequent to formation, and not primarily produced by other processes such as photochemistry, our yields  $G$  can be used along with the energy deposition rates of Paper I to compute production fluxes for Titan's atmosphere. If in addition we adopt some model for the turbulent (eddy) diffusion of these molecules, column densities in the atmosphere can be computed.

While the auroral production zone extends over at least hundreds of kilometers, it is well-separated from the sink: all of the molecules produced will freeze out as condensate hazes at altitudes of about 40–250 km above the surface (see Paper I, Figs. 8–11, for  $\alpha = 1$ ), and those we consider here all condense below 120 km. Magnetospheric electrons penetrate to about 300 km. We therefore adopt a simple model in which production takes place at high altitudes, the molecular products mix downward through several scale heights  $H$ , and are removed by a sink at altitude  $z_0$ . From Strobel (1983) we use

$$N_i = \frac{4H_a^2\phi_i}{K_{\min}} \quad (1)$$

where  $N_i$  is the atmospheric column density (molec cm<sup>-2</sup>) for a species supplied from above at flux  $\phi_i$  in an atmosphere with scale height  $H_a$  and minimum eddy diffusion coefficient  $K_{\min}$  at  $z_0$ . This expression results if (as is often assumed) the scale height for increase of  $K$  with altitude is equal to twice the atmospheric scale height (i.e.,  $K \propto (\text{density})^{-1/2}$ ; see Strobel 1983, Yung *et al.* 1984).

Yung *et al.* (1984) adopted a  $K(z)$  profile which decreases abruptly to 300 cm<sup>2</sup> sec<sup>-1</sup> at  $z = 150$  km and stays constant to the surface. Since all species condense below 120 km, we adopt  $K_{\min} = 300$  cm<sup>2</sup> sec<sup>-1</sup>. While  $K_{\min}$  is constant, we evaluate  $H_a$  at the (approximate) altitude where condensation actually occurs (Paper I, Table V). The molecular flux  $\phi_i = FG_i$ , where  $G_i$  is the radiation yield and  $F$  is the altitude-integrated radiation flux. With  $H_a = RT/\bar{\mu}g$ , we have

$$N_i = \frac{4H_a^2FG_i}{K_{\min}} = \left(\frac{2RT}{\bar{\mu}g}\right)^2 \frac{FG_i}{K_{\min}}, \quad (2)$$

where  $R$  is the cgs gas constant per mole,  $T$  is the temperature at the appropriate condensation altitude,  $g$  is the gravitational acceleration, and  $\bar{\mu}$  is the mean molecular mass. Variations being small compared to other uncertainties, we adopt  $g \approx 134$  cm sec<sup>-2</sup> and  $\bar{\mu} \approx 29$ . The effective mole fraction of gas  $i$  is then

$$X_i = \frac{N_i}{N} = \frac{\bar{\mu}g}{A_0p} N_i, \quad (3)$$

where  $p$  is the local pressure and  $A_0$  is Avogadro's number.

We use the experimental results for 0.24 mbar and the above equations to compute the expected column densities and mole fractions, for the gases listed in Table II, in Titan's atmosphere. In Table V we present these results, and compare predicted abundances for those molecules detected on Titan with those determined in early analyses of the Voyager IRIS data. We also compare with the results of the Yung *et al.* (1984) model, which is basically a photochemical and chemical-kinetic model with eddy mixing, but which additionally incorporates nitrogen chemistry by adopting an N<sub>2</sub> dissociation rate (by electrons) of  $1 \times 10^9$  cm<sup>-2</sup> sec<sup>-1</sup>. [This rate was derived from Voyager EUV airglow observations by Strobel and Shemansky (1982), and applies primarily to  $z \geq 1000$  km.] The Yung *et al.* results are mean mole fractions above  $z = 45$  km; for their results  $N_i = 1.9 \times 10^{25} X_i$  (cf. their Table 5A). By identifying the base pressure levels  $p$  assumed in determining mole fractions in early analyses of the Voyager IRIS data (primarily Kunde *et al.* 1981, Maguire *et al.* 1981), we can compute the corresponding column density  $N_i$ :

$$N_i = NX_i = \frac{pA_0}{\bar{\mu}g} X_i. \quad (4)$$

Values for  $N_i$  are listed alongside our estimated condensation pressures.

We list a range of computed  $N_i$  and  $X_i$  values spanning two assumptions for  $F$ . The lower value ( $F = 1.5 \times 10^{10}$  eV cm<sup>-2</sup> sec<sup>-1</sup>) corresponds to the integrated flux for magnetospheric electrons only, while the higher ( $F = 7.5 \times 10^{10}$  eV cm<sup>-2</sup> sec<sup>-1</sup>) sums all charged particle energy sources listed in Table 4 of Paper I.

Since our estimates include no photochemical input, they will, of course, greatly underestimate molecules known to be primary photochemical products. It is no surprise that this is the case for C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub>. On the other hand, it is remarkable that our predicted values agree with the Voyager observations for four of the six other compounds, HCN, NCCN, HC<sub>2</sub>CN, and C<sub>4</sub>H<sub>2</sub>, and are within a factor of 2 for C<sub>2</sub>H<sub>2</sub> and C<sub>3</sub>H<sub>4</sub>. In fact, the overall agreement with observation for these six compounds is better than that of the Yung *et al.* model. [Note also that seemingly good agreement of  $X_i$ 's between the Yung *et al.* model and observations is an artifact resulting from their use of  $z = 45$  km ( $p \approx 100$  mb) as the base level for all molecules; the corresponding  $N_i$ 's are too high, especially for C<sub>2</sub>H<sub>2</sub> and HCN.] Furthermore, in our results there are no spurious molecules which conflict with the Voyager observations; every molecule for which we compute  $X_i > 10^{-8}$  is in fact found on Titan. Of course, it is possible that a very thorough search could find some of the molecules predicted to have lower abundances,

TABLE V  
Production Rates and Abundances of Stratospheric Organic Gases

Molecule	$G$ , molec/heV	$\phi$ , $\text{cm}^{-2} \text{s}^{-1}$	$p_{\text{cond}}$ , mbar: This Work (IRIS)	IRIS Observed <sup>a</sup> ( $X_i$ , $N_i$ )	Chemical Model <sup>b</sup> ( $X_i$ , $N_i$ )	This Work ( $X_i$ , $N_i$ )
$\text{CH}_3\text{-CH}_3$	$8.1 \times 10^{-2}$	$1.2 \times 10^7$	45 (50)	$2 \times 10^{-5}$ $1.6 \times 10^{20}$	$1.7 \times 10^{-5}$ $3.2 \times 10^{20}$	$0.6\text{-}3.2 \times 10^{-7}$ $0.5\text{-}2.3 \times 10^{18}$
$\text{CH}_3\text{-CH}_2\text{-CH}_3$	$1.2 \times 10^{-2}$	$1.8 \times 10^6$	28 (50)	$4 \times 10^{-6}$ $3.2 \times 10^{19}$	$7.9 \times 10^{-7}$ $1.5 \times 10^{19}$	$0.3\text{-}1.3 \times 10^{-7}$ $1.2\text{-}6.1 \times 10^{17}$
$\text{HC}\equiv\text{CH}$	$1.6 \times 10^{-1}$	$2.4 \times 10^7$	32 (50)	$2 \times 10^{-6}$ $1.6 \times 10^{19}$	$4.0 \times 10^{-6}$ $7.6 \times 10^{19}$	$0.3\text{-}1.3 \times 10^{-6}$ $1.3\text{-}6.7 \times 10^{18}$
$\text{HC}\equiv\text{N}$	$3.3 \times 10^{-2}$	$5.0 \times 10^6$	18 (10)	$2 \times 10^{-7}$ $3.2 \times 10^{17}$	$5.6 \times 10^{-7}$ $1.1 \times 10^{19}$	$1.8\text{-}9.0 \times 10^{-7}$ $0.5\text{-}2.6 \times 10^{18}$
$\text{CH}_2=\text{CH}_2$	$9.0 \times 10^{-2}$	$1.4 \times 10^7$	140 (50?)	$4 \times 10^{-7}$ $3.2 \times 10^{18}$	$3.3 \times 10^{-8}$ $6.3 \times 10^{17}$	$0.2\text{-}1.0 \times 10^{-7}$ $0.4\text{-}2.2 \times 10^{18}$
$\text{N}\equiv\text{C-C}\equiv\text{N}$	$3.6 \times 10^{-3}$	$5.4 \times 10^5$	22 (20)	$10^{-7}\text{-}10^{-8}$ $3 \times 10^{17}\text{-}3 \times 10^{16}$	$1.9 \times 10^{-8}$ $3.6 \times 10^{17}$	$1.4\text{-}7.0 \times 10^{-8}$ $0.5\text{-}2.4 \times 10^{17}$
$\text{HC}\equiv\text{C-C}\equiv\text{N}$	$2.4 \times 10^{-3}$	$3.6 \times 10^5$	16 (20)	$10^{-7}\text{-}10^{-8}$ $3 \times 10^{17}\text{-}3 \times 10^{16}$	$5.6 \times 10^{-8}$ $1.1 \times 10^{18}$	$1.6\text{-}8.0 \times 10^{-8}$ $0.4\text{-}2.0 \times 10^{17}$
$\text{CH}_3\text{-C}\equiv\text{N}$	$1.5 \times 10^{-3}$	$2.2 \times 10^5$	~20	----	----	$0.7\text{-}3.2 \times 10^{-8}$ $0.2\text{-}1.0 \times 10^{17}$
$\text{CH}_3\text{-C}\equiv\text{CH}$	$1.4 \times 10^{-3}$	$2.0 \times 10^5$	29 (50)	$3 \times 10^{-8}$ $2 \times 10^{17}$	$1.8 \times 10^{-7}$ $3.4 \times 10^{18}$	$0.3\text{-}1.4 \times 10^{-8}$ $1.3\text{-}6.5 \times 10^{16}$
$\text{CH}_2=\text{CH-CH}=\text{CH}_2$	$1.3 \times 10^{-3}$	$2.0 \times 10^5$	~20	----	----	$0.6\text{-}3.0 \times 10^{-8}$ $1.9\text{-}9.5 \times 10^{16}$
$\text{HC}\equiv\text{C-C}\equiv\text{CH}$	$8.2 \times 10^{-4}$	$1.2 \times 10^5$	20 (20)	$10^{-7}\text{-}10^{-8}$ $3 \times 10^{17}\text{-}3 \times 10^{16}$	$7.8 \times 10^{-10}$ $1.5 \times 10^{16}$	$0.4\text{-}1.8 \times 10^{-8}$ $1.2\text{-}6.0 \times 10^{16}$
$\text{CH}_2=\text{C}=\text{CH}_2$	$7.7 \times 10^{-4}$	$1.2 \times 10^5$	~30	----	$5.0 \times 10^{-9}$ $9.5 \times 10^{16}$	$1.5\text{-}7.5 \times 10^{-9}$ $0.7\text{-}3.6 \times 10^{16}$
$\text{CH}_2=\text{CH-C}\equiv\text{CH}$	$2.4 \times 10^{-4}$	$3.6 \times 10^4$	~20	----	----	$1.1\text{-}5.5 \times 10^{-9}$ $0.3\text{-}1.7 \times 10^{16}$
$\text{CH}_2=\text{CH-C}\equiv\text{N}$	$1.9 \times 10^{-4}$	$2.8 \times 10^4$	~20	----	----	$0.8\text{-}4.1 \times 10^{-9}$ $0.3\text{-}1.3 \times 10^{16}$
$\text{CH}_3\text{-CH}=\text{CH}_2$	$9.3 \times 10^{-5}$	$1.4 \times 10^4$	~30	----	$\sim 1 \times 10^{-8}$ $\sim 2 \times 10^{17}$	$0.3\text{-}1.3 \times 10^{-9}$ $0.8\text{-}4.2 \times 10^{15}$
$\text{C}_3\text{H}_3\text{N} (?)$	$5 \times 10^{-5}$	$8 \times 10^3$	~20	----	----	$0.2\text{-}1 \times 10^{-9}$ $0.7\text{-}4 \times 10^{15}$
$\text{CH}_3\text{-CH}_2\text{-C}\equiv\text{N}$	$4 \times 10^{-5}$	$6 \times 10^3$	~20	----	----	$0.2\text{-}1 \times 10^{-9}$ $0.6\text{-}3 \times 10^{15}$
1- <i>H</i> -tetraazole (?)	$3 \times 10^{-5}$	$4 \times 10^3$	~20	----	----	$1\text{-}6 \times 10^{-10}$ $0.4\text{-}2 \times 10^{15}$
$\text{CH}_3\text{N}_3 (?)$	$3 \times 10^{-6}$	$4 \times 10^2$	~20	----	----	$1\text{-}6 \times 10^{-11}$ $0.4\text{-}2 \times 10^{14}$

<sup>a</sup> Kunde *et al.* (1981); Maguire *et al.* (1981); propane: R. E. Samuelson, personal communication, 1983.

<sup>b</sup> Values from Yung *et al.* (1984), Table 5A; propene estimated using their Fig. 7a.

depending on the details of their spectra. Some of the molecules, especially dinitriles, found in experiments at lower  $X_{\text{CH}_4}$  (Thompson *et al.* 1989) may also be present.

In Table VI and Fig. 6 we present a concise comparison of our results and those of Yung *et al.* with the equatorial and polar abundances of hydrocarbons and nitriles re-

cently derived by Coustenis *et al.* (1989) and Coustenis (1989). Here the "photochemical model"  $X_i$ 's from Yung *et al.* (1984) are read directly from their figures (4a, 6a, 7a, and 8a) at the  $z \approx 115 \pm 10$  km appropriate to the 4.5–8.5 mbar pressure range encompassing the levels of maximum thermal radiance contribution in the IRIS-de-

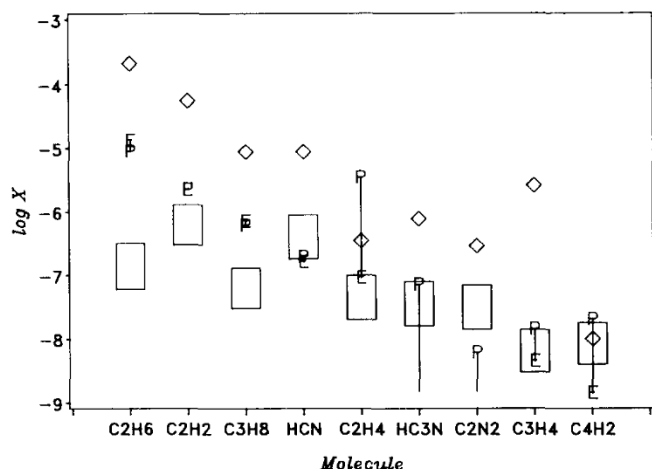


FIG. 6. Comparison of the mole fraction range computed from our laboratory plus eddy mixing model (large rectangles) and mole fractions read from the figures of Yung *et al.* (1984) (diamonds) with the Voyager IRIS-derived values determined for Titan's equatorial region (Coustenis *et al.* 1989) and polar region (Coustenis 1989). The equatorial and polar mole fractions are marked, respectively, by the letters E and P, and connected by a tie line to indicate the equatorial to polar range.

tected molecular bands of minor species (Coustenis *et al.* 1989). These  $X_i$ 's are more appropriate for comparison with our results and with IRIS-derived results than are the values listed in Table V. The photochemical model results are generally too high (as can be seen in our Fig. 6 or by comparing the vertical profiles in Yung *et al.*'s figures with those in Fig. 7 of Coustenis *et al.*), and in most cases agree less well with the observations than do our results. The Yung *et al.* predictions agree within a factor of 5 of the Voyager-derived abundances for only two molecules out of nine; while our computed range (also a factor of 5) overlaps the Voyager-derived abundances for five molecules out of nine. Even an arbitrary scaling of the Yung *et al.* results by  $10^{-1.33}$  (the optimal shift in a

least-squares sense) produces an agreement which is only comparable to, not better than, ours. The results of an updated model by Yung (1987) in which an alternate scheme for nitrile production was proposed are not significantly different. [The update was required because the key step for C<sub>2</sub>N<sub>2</sub> production in Yung *et al.* (1984) was found to have a rate 2000 times less than that which Yung *et al.* adopted in order to explain the C<sub>2</sub>N<sub>2</sub> abundance.]

While our results should be augmented with further laboratory work (at lower  $p$  and  $X_{\text{CH}_4}$ ), the agreement is so good that we can draw two immediate conclusions: first, this is a clear demonstration that *properly designed laboratory experiments can yield results directly applicable to planetary atmospheres*, at a level of application much higher than that at which laboratory work on elementary chemical kinetic steps, for example, is incorporated into photochemical models. This is especially true for radiation-chemical processes, which operate via small plasma blobs produced (mostly) near the termini of secondary electron paths (regardless of the nature of the original exciting entity—see Thompson *et al.* 1987). Models including *only* photochemistry are *inherently insufficient* to describe planetary environments where a significant charged particle radiation source is available (particularly true at large heliocentric distances). Both the inhomogeneous nature of charged particle processes and the omission of those steps which cannot occur photochemically prevent such models from representing the physical situation accurately. An approach such as that of Yung *et al.* (1984), where simple electron-dissociation products (N atoms) are assumed to be uniformly mixed in the gas, is a welcome attempt to include charged particle radiation, but still cannot describe the *local* plasma processes characteristic of chemical synthesis in a radiation environment.

Second, the agreement suggests that the *as-yet-undetected* molecules found in our 0.24 mbar experiment are probably present in Titan's atmosphere with abundances

TABLE VI  
Comparisons of Observed and Computed Mole Fractions<sup>a</sup>

Molecule	$p_{\text{cond}}$ , mbar equat./polar	Chemical model	Observed, equatorial	Observed, polar	This work
C <sub>2</sub> H <sub>6</sub>	38/47	$2.1 \times 10^{-4}$	$1.3 \times 10^{-5}$	$8.8 \times 10^{-6}$	$0.6-3.2 \times 10^{-7}$
C <sub>2</sub> H <sub>2</sub>	29/32	$5.6 \times 10^{-5}$	$2.2 \times 10^{-6}$	$2.2 \times 10^{-6}$	$0.3-1.3 \times 10^{-6}$
C <sub>3</sub> H <sub>8</sub>	29/31	$8.8 \times 10^{-6}$	$7.0 \times 10^{-7}$	$6.0 \times 10^{-7}$	$0.3-1.3 \times 10^{-7}$
HCN	16/15	$8.8 \times 10^{-6}$	$1.6 \times 10^{-7}$	$1.9 \times 10^{-7}$	$1.8-9.0 \times 10^{-7}$
C <sub>2</sub> H <sub>4</sub>	140/77	$3.5 \times 10^{-7}$	$9.0 \times 10^{-8}$	$3.4 \times 10^{-6}$	$0.2-1.0 \times 10^{-7}$
HC <sub>3</sub> N	-/20	$7.8 \times 10^{-7}$	$<1.5 \times 10^{-9}$	$7.0 \times 10^{-8}$	$1.6-8.0 \times 10^{-8}$
C <sub>2</sub> N <sub>2</sub>	-/28	$2.9 \times 10^{-7}$	$<1.5 \times 10^{-9}$	$6.0 \times 10^{-9}$	$1.4-7.0 \times 10^{-8}$
C <sub>3</sub> H <sub>4</sub>	29/28	$2.6 \times 10^{-6}$	$4.4 \times 10^{-9}$	$1.4 \times 10^{-8}$	$0.3-1.4 \times 10^{-8}$
C <sub>4</sub> H <sub>2</sub>	24/24	$1.0 \times 10^{-8}$	$1.4 \times 10^{-9}$	$2.0 \times 10^{-8}$	$0.4-1.8 \times 10^{-8}$

<sup>a</sup> Sources: "Chemical Model," read from Figs. 4a, 6a, 7a, and 8a of Yung *et al.* (1984); "Observed, Equatorial," Coustenis *et al.* (1989); "Observed, Polar," Coustenis (1989).

near those we derive; they will also produce condensate hazes at 40–100 km altitude, as do the Voyager-detected species. We submit one note of caution: obviously, our model would agree even better if even a simple treatment of photochemistry (photolysis and production rates) were included. In particular, molecules that are particularly susceptible to long-wavelength UV photodissociation (such as  $\text{H}_2\text{CCHCHCH}_2$ , butadiene) should have abundances lower than we calculate. Nonetheless, we expect the eventual discovery of  $\text{CH}_3\text{CN}$ ,  $\text{H}_2\text{CCHCHCH}_2$ ,  $\text{H}_2\text{CCCH}_2$ ,  $\text{CH}_2\text{CHCN}$ ,  $\text{CH}_3\text{CHCH}_2$ ,  $\text{CH}_3\text{CH}_2\text{CN}$ , and perhaps even the curious ring compound 1-*H*-tetraazole, methyl azide ( $\text{CH}_3\text{N}_3$ ), and an unidentified compound whose formula seems to be  $\text{C}_3\text{H}_3\text{N}$ .

Using Voyager IRIS spectra, Cerceau *et al.* (1985) derived upper limits for the several undetected nitriles found in laboratory experiments at  $p \approx 30$  mb. These upper limits, and our predicted mole fractions, are listed in Table VII. Cerceau *et al.* also estimated mole fractions for these molecules based on the laboratory results available at that time. For all of the molecules listed in Table VII they predicted  $X_i \geq 2.5 \times 10^{-7}$ . Because our results show that yields of many molecules decrease rapidly between 17 mbar and 0.24 mb, our estimates of the mole fractions of currently undetected molecules in Titan's atmosphere are much less than those of Cerceau *et al.* Detection of even the more abundant of these molecules requires new spectroscopy of very high signal-to-noise ratio and/or future measurements by the Cassini orbiter and Huygens probe.

Finally, we take a retrospective look at the conjectures in Paper I regarding the possible abundances of some organic compounds in Titan's stratosphere. At that time we had not yet initiated more direct experiments such as those reported here, but had results for the sequential vacuum pyrolysis products of a  $\text{CH}_4\text{-NH}_3\text{-H}_2\text{O}$  tholin (Khare *et al.* 1981) and preliminary results for the same procedure applied to  $\text{N}_2 + \text{CH}_4$  tholin (Khare *et al.* 1982, 1984b, Sagan *et al.* 1985). Species adsorbed or otherwise

loosely bound in the tholin would be released in quantity at low temperatures, while small amounts of high-temperature pyrolyzates could be produced on Titan by radiation impinging on slowly sedimenting tholin haze. We list the compounds from the 0.24 mbar experiment with  $(\text{C} + \text{N}) \geq 3$  in Table VII, along with the extrapolated abundances for  $\alpha = 1$  (relevant to the current case) from Figs. 10–11 of Paper I. Three of these predictions are within or very close to the range of the 0.24-mbar experimental results, the other two are off by factors of about 10 and 100. In fact, only two of the abundant pyrolyzates in Fig. 10d of Paper I (1-butene and *trans*-2-butene) are not found among the experimental products. ( $\text{NH}_3$  is not included in Table II but has been found in our preliminary analysis of more recent  $\text{N}_2 + \text{CH}_4$  flow experiments, as have  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_3\text{H}_8$ .) This rough agreement between gas-phase products and solid-phase pyrolyzates is further evidence that at least the small-molecule component of the pyrolyzates does not derive entirely from thermal rearrangement of the solid (Khare *et al.* 1981, Sagan *et al.* 1985) and suggests some promise for attempts (Thompson and Sagan 1989) to connect gas phase chemistry with tholin synthesis and composition.

## V. LABORATORY AND COMPUTATIONAL SIMULATIONS: COMMENTS

We have demonstrated that current technology permits laboratory experiments which quantitatively simulate molecular synthesis in real (and chemically complex) planetary atmospheres, especially for the case of charged-particle-induced chemistry, where the nature of the energy deposition process involves plasma chemistry which can, with some effort, be modeled in the laboratory. In this light, some previous criticisms regarding the applicability of "simulation" experiments to real planetary atmospheres are in need of reevaluation. For example, Atreya

TABLE VII  
Comparison of Previous Abundance Estimates with Current Results

Species	Extrapolated experimental estimate <sup>a</sup>	Extrapolated pyrolyzate estimate, $\alpha = 1^b$	Predicted abundance this work	Voyager IRIS upper limit <sup>a</sup>
$\text{CH}_3\text{-C}\equiv\text{N}$	$1 \times 10^{-6}$	$1 \times 10^{-8}$	$0.6\text{--}3.2 \times 10^{-8}$	$<2.5 \times 10^{-7}$
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	—	$1 \times 10^{-10}$	$0.6\text{--}3.0 \times 10^{-8}$	—
$\text{CH}_2=\text{C}=\text{CH}_2$	—	—	$1.5\text{--}7.5 \times 10^{-9}$	—
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	—	—	$1.1\text{--}5.5 \times 10^{-9}$	—
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	$5 \times 10^{-7}$	$1 \times 10^{-9}$	$0.8\text{--}4.1 \times 10^{-9}$	$<2.0 \times 10^{-7}$
$\text{CH}_3-\text{CH}=\text{CH}_2$	—	$1 \times 10^{-8}$	$0.3\text{--}1.3 \times 10^{-9}$	—
$\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{N}$	$5 \times 10^{-7}$	$1 \times 10^{-9}$	$0.2\text{--}0.9 \times 10^{-9}$	$<5.0 \times 10^{-7}$
$\text{CH}_3-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$	$2.5 \times 10^{-7}$	—	$<1 \times 10^{-9}$	$<2.5 \times 10^{-7}$
$\text{C}_3\text{H}_5-\text{C}\equiv\text{N}$ isomers	$12.5 \times 10^{-7}$	—	$<1 \times 10^{-9}$	$\leq 5 \times 10^{-8}$

<sup>a</sup> Cerceau *et al.* (1985).

<sup>b</sup> Sagan and Thompson (1984).

(1986) states: "Because of physical limitations, these laboratory experiments cannot truly simulate planetary conditions. For example, the extremely low pressures where the energy is deposited on Titan cannot be used effectively in the laboratory simulation experiments. The actual energy deposited in Titan's atmosphere is generally much lower than that from laboratory irradiating sources. Furthermore, at Titan, the energy is available for billions of years, a condition the laboratory experiments cannot simulate." While these objections may have applied to most or all of the experiments performed to that date, they are not *categorically* true. We are obviously at the threshold of pressures sufficiently low as to be directly applicable to magnetospheric electron deposition zones on Titan and elsewhere. The agreement between experiment and observation reported here indicates that the pressures are (in practice) already sufficiently low, although the drastic changes from 17 mbar to 0.24 mbar accentuate the fact that no previous laboratory experiments have quantitatively explored this low-pressure regime. Atreya's objection about actual energy deposition (rates) can be inverted: as noted above, much of the chemistry in charged particle radiation occurs locally along ion trails and at terminal plasma blobs. This is precisely why traditional photochemical models cannot truly simulate planetary conditions, even if they include simple radiation-chemical species as inputs. Finally, the remark about long-timescale irradiation fails to mention diffusive transport and sedimentation (which are of course key to atmospheric chemical models of all types), which will typically remove the chemical products from the altitude zone of high radiation flux. The most important applicability requirement is that the irradiation rate be kept within the low-dose limit: that is, the probability that a second particle track will cross a still "hot" one on chemical reaction (sometimes, diffusion) timescales must be negligible. In some cases solid-state diffusion can impose more restrictive criteria, but often a 10<sup>6</sup> year planetary radiation dose can be delivered within 1 day to 1 hr in the laboratory without violating any significant constraints on rate. Billion year-equivalent radiation times could then be achieved in as little as 4 months.

Experiments have sometimes been applied out of context, or the techniques have been insufficient to achieve conditions directly relevant to planetary environments, or analytical techniques have been insufficiently sensitive or quantitative. But these shortcomings can be corrected. Computer photochemical kinetic models are important and continue to improve, but still exhibit problems of incompleteness, inadequately known rate constants, and limited complexity (in number and size of molecular species). While they have their own difficulties, laboratory experiments are not subject to these problems. Both methods should be pursued in concert as complementary ap-

proaches to the same questions (Sagan *et al.* 1984). In particular, experiments employing continuous-flow, low-dose, and sufficiently large reaction volume/area ratios (or another method of wall isolation) for a given low pressure are very relevant to radiation-chemical (charged-particle-induced) processes in planetary atmospheres. We hope to push back further the frontiers of low pressure and low reactant mole fraction in future work.

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