Analysis of the Time-Dependent Chemical Evolution of Titan Haze Tholin

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Haze particles exert a significant influence over the thermodynamics and radiation absorption properties of the Titan haze, as well as its complex organic chemistry. Characterization of both the molecular and the submicrometer components of the haze is therefore vital for understanding the global properties of Titan. We have carried out a Titan tholin synthesis experiment and measured the time variation of the infrared spectrum of the product as a thin film developed. Also, to examine the possibility of oxygen contamination, we compared the infrared spectrum of the tholin film with that of a tholin film exposed to dry air and laboratory air. The objective of this study is to understand the chemical processes related to how simple organic molecules are processed into more complex haze particles. The progressive development of features characteristic of amines, aromatic and aliphatic hydrocarbons, and nitriles in the experimental mixture is clear. Of particular interest is the formation of aromatic rings after only a few seconds of glow discharge, indicating that these compounds appear to be intermediates between simple haze molecules and microphysical aerosols. The early dominance of aromatic ring structures is accompanied during the later stages of the experiment by the appearance of nitrile and amine compounds. This time-dependent succession of chemical structures provides vital clues to the possible chemical formation pathways of Titan haze aerosols. ©c 2002 Elsevier Science (USA)

Key Words: Titan; tholins; stratospheric chemistry; aromatics; amines; alkanes; hydrocarbons; aerosols.

1. INTRODUCTION

Observations of Titan's haze by Voyager indicate a dense layer of smog produced by ongoing charged particle photochemistry and ultraviolet (UV) radiation in Titan's stratosphere (Hanel *et al.* 1981). Titan's atmospheric haze dominates its temperature, atmospheric circulation, and climate control, and photochemistry plays a key role in the structure and evolution of the haze. Detailed knowledge of Titan's photochemistry provides a deeper understanding of its global properties (Coustenis *et al.* 1991). This laboratory study of the Titan haze simulates a detailed time-dependent evolution of organic compounds in the haze in an attempt to closely trace how simple organic molecules are processed into more complex haze particles, termed "tholins." A laboratory polarimetric determination of the wavelength-dependent real part of the refractive index of synthesized Titan tholin gave 1.65 ± 0.05. These refractive indices are consistent with those deduced for the Titan aerosols from Earth-based observations (Rages and Pollack 1980), from Pioneer 11 observations (Tomasko and Smith 1982), and from Voyager observations (Rages and Pollack 1983, Rages *et al.* 1983). Subsequent laboratory work (Khare *et al.* 1982, 1984a) showed that the real and imaginary values of the complex refractive indices of these materials are in excellent agreement with those derived for the Titan aerosols. In short, laboratory studies

of complex organic tholins have shown that these materials produce an excellent match to the optical properties of the Titan haze (Khare *et al.* 1984a,b, Khare *et al.* 1994, Ferris and Clarke 1995, Clarke and Ferris 1997a,b). In particular, Khare *et al.* (1984a) reported the optical constants of tholins, produced by UV irradiation and charged particle bombardment of molecular nitrogen (N_2) and methane (CH_4) mixtures simulating the titanian atmosphere. Spectroscopic measurements were performed in ambient air, and the detection of carbon dioxide CO_2 and carbon monoxide CO in gas chromatograph mass spectrometry (GC/MS) of this material has raised concerns about possible effects on the spectra of oxygen-containing compounds introduced postsynthesis. For instance, electron microprobe analysis indicated the presence of some oxygen atoms at the surface of the Titan tholin and much less a few monolayers deep into the surface. Understanding how tholins evolve and determining their structural components is of vital importance in clarifying the nature of the Titan haze. The experiments described in this paper aid our understanding of these mechanisms.

In Section 2, we describe theoretical evidence for heterocyclics in the Titan haze, based on ab initio quantum chemical calculations; in Section 3, we describe our experimental objectives and techniques for the synthesis of solid tholin material. In Section 4, we describe and discuss our results for solid tholins, while in Section 5, we describe complementary experimental objectives and techniques from separate and previously unpublished work on the gas-phase products of Titan tholin analog synthesis and comment on how these investigations may yield clues about the structural monomers of tholins. In Section 6, we present our results and discussion for gas-phase products. Finally, in Section 7, we make our conclusions and recommendations for future experimental work on the Titan haze.

2. THEORETICAL EVIDENCE FOR AROMATIC FORMATION IN THE TITAN HAZE

Current photochemical models of Titan, Saturn's largest satellite, include chemical reactions producing molecules composed of up to six carbon atoms and then extrapolate straight to aerosols, such as tholins (Yung *et al.* 1984, Toublanc *et al.* 1995). Ricca *et al.* (2001) have derived evidence for polycyclic aromatic hydrocarbon synthesis in the Titan haze via ab initio quantum chemical computations. Their paper presents preliminary work on reactions that produce nitrogenated aromatic molecules containing up to 12 nonhydrogen atoms. This helps bridge the gap between the small molecules and the aerosols and hence improves the current knowledge of Titan's stratospheric chemistry. They have determined the barriers and reaction energies for the incorporation of nitrogen into the rings of polycyclic aromatic hydrocarbons (PAHs). The largest activation barrier is still less than 15 kcal mol^{-1}, easily surmountable by input of UV photon energy typically present in the Titan haze. Pure and nitrogenated PAH formation is viable for the haze provided there is enough energy to initiate the reaction sequence by the removal of an

H atom from benzene ($\sim$11 kcal/mol or 0.5 eV) or the breakage of a C–H bond (99 kcal/mol or 4.31 eV). The UV radiation in the Titan haze has wavelengths of 1500 Å and longer (or 8.05 eV and less), due to shorter wavelengths being absorbed by CH_4 and N_2. However, this provides more than enough energy to supply these reactions sufficiently. Reaction barriers following initiation are of the order of several kcal per mole and can thus be powered by the UV radiation filtering through the haze described by Courtin *et al.* (1991). Since the typical temperature of the haze varies from 70 to 175 K ($\leq$0.35 kcal/mol), the macromolecular chemistry of the Titan haze is predominantly photochemically, not thermally, driven. In summary, from these energetics-based arguments, both pure and nitrogenated PAH formation is expected, to occur under the conditions present in the atmosphere of Titan. Finally, Bakes *et al.* (2002) have incorporated the effects of the charging of pure and nitrogenated heterocyclics on the chemistry, conductivity, thermodynamics, and aerosol agglomeration processes occurring in the Titan haze. If pure and nitrogenated PAHs are found to exist in the Titan haze by the Cassini mission, the effects for these processes are highly significant because PAHs are efficient absorbers of UV radiation, are highly electrophilic, and provide a large surface area for ongoing haze chemistry. This paper presents strong experimental evidence for the existence of heterocyclic aromatics in the Titan haze as part of the building blocks of Titan tholin analogs, and our results are detailed in the following sections.

3. SOLID THOLIN SYNTHESIS

3.1. Experimental Objectives

The objective of this study is to explore the time-dependent chemical evolution of Titan tholins in an oxygen-free environment and to then study possible modification of the synthesized laboratory tholins due to their exposure to (1) dry and (2) laboratory air. We have made a time-dependent analysis of the Titan tholin analogs from 0 to 60 h. From this, we can clarify the nature of the building blocks of Titan tholin and eliminate concerns about sample pollution in former simulations. Prior studies with an electron microprobe have indicated the presence of oxygen atoms at the surface of the tholin with fewer oxygen atoms residing a few monolayers deep into the tholin surface. This raised concerns about a possible degree of error in the measurement of the tholin optical constants, since all measurements were made in the presence of laboratory air. To solve this possible problem, we have studied the infrared (IR) spectrum of a film which has not been exposed to air, and we have then exposed the sample, in turn, to the dry air and laboratory air compounds mentioned previously.

3.2. Experimental Method For Solid Tholin

We constructed an IR cell with two CsI windows (as shown in Fig. 1). The cell was subjected to a cyclic induction electrical glow discharge powered by a tesla coil, model BD-10, supporting $\sim$10–15 kV at frequencies of $\sim$0.5 MHz. A mixture of
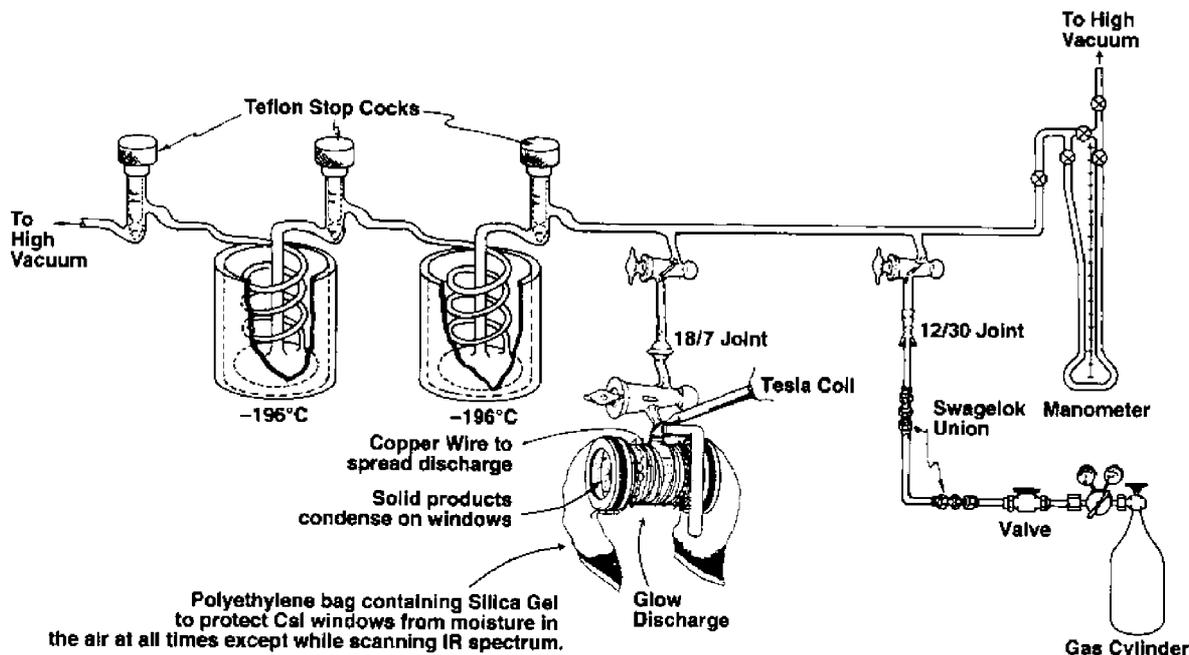
FIG. 1. The glow discharge apparatus used to synthesize solid tholin material over a period of 60 h. $N_2 + CH_4$ gas is introduced from the tank of gas at the right and an inductive glow discharge is excited by a tesla coil as the gas flows through the discharge tube. Solid products condense on the windows of the glow discharge apparatus and their IR spectrum is taken at various time intervals. Unreacted gas is pumped out of the apparatus via the high vacuum source on the left.

90% N_2 and 10% CH_4 was introduced into the cell and the pressure in the cell was maintained at 71 mbar of mercury, relevant to the atmospheric chemistry induced by cosmic rays in Titan's troposphere. All phases of the experiment were conducted in oxygen-free conditions. The supply of CH_4 was replenished periodically to simulate the reservoir of methane in Titan's upper atmosphere. The IR spectra were produced via glow discharge; this method is better than the more localized method of electrical discharge, which does not effectively simulate the lower temperatures achieved via cosmic ray irradiation. Spectra were taken periodically throughout the experiment. These spectra included gas-phase species. We used a Perkin–Elmer model 621 grating spectrophotometer and replenished with the original N_2/CH_4 mixture; this procedure was repeated 32 times. The cyclic discharge consisted of 2 min of applied voltage followed by 4 min of no discharge to cool the tesla coils. The methane in the cell was all but depleted in only 2h, and during the replenishment step, we evacuated any remaining CH_4, N_2, and H_2 which might have evolved from the mixture, while retaining any condensible product gases at liquid N_2 temperature (77 K) by cooling the tubing extending out of the IR cell in Fig. 1. This resulted in a small increase in pressure from cycle to cycle as the gases were held in liquid N_2 during each CH_4/N_2 fill to approximately 71 mbar and then allowed to reequilibrate in the gas phase. However, this increase was probably minimal, as the cell's ability to sustain a glow discharge was not greatly degraded. Once the anaerobic phase of the experiment was finished, we exposed the sample to air and compared the resulting spectra to the anaerobic results.

4. RESULTS AND DISCUSSION FOR SOLID THOLIN MATERIAL

Figure 2 shows the final spectrum produced after 32 refill cycles and 60 h of total cycle time, with residual gases removed. The Titan haze synthesis described in the previous sections produces a wealth of organic molecules, including alkanes, alkenes, aromatic ring hydrocarbons, nitriles, amines, and various side-groups such as C–H and N–H (Khare *et al.* 1982, 1984b). Our final IR spectrum is in good agreement with the IR spectra of tholin produced by spark discharge in a closed system (Sagan and Thompson 1984).

The initial gas mixture displays prominent methane features around 3030 cm^{-1} (3.3 μm) and 1429–1250 cm^{-1} (7–8 μm). Most of the spectral features appeared quickly, after only 1 h and all salient features were apparent after 8 h. Amines show up at 3333 cm^{-1} (3.0 μm) as stretch vibrations of N–H single bonds and again at 1613 cm^{-1} (6.2 μm) and ~750 cm^{-1} (~13 μm) as N–H single bond bending modes. These wavelengths also indicate polycyclic aromatic hydrocarbons, specifically the aromatic C–H stretch at 3030 cm^{-1} (3.3 μm) and the aromatic C–C stretch at 1613 cm^{-1} (6.2 μm). There is also evidence for C–N stretching around 1111 cm^{-1} (9 μm). Alkanes and alkenes, with singly and doubly bonded carbons, have a peak at 2950 cm^{-1} (3.39 μm) via C–H stretching and another at 1149 cm^{-1} (8.7 μm) with C–C stretching vibrations. The peak around 2151 cm^{-1} (4.65 μm) is caused by triply bonded CN nitrile stretch vibrations. One of the earliest features to emerge was a very strong absorption feature at ~1351 cm^{-1} (7.4 μm), which we ascribed
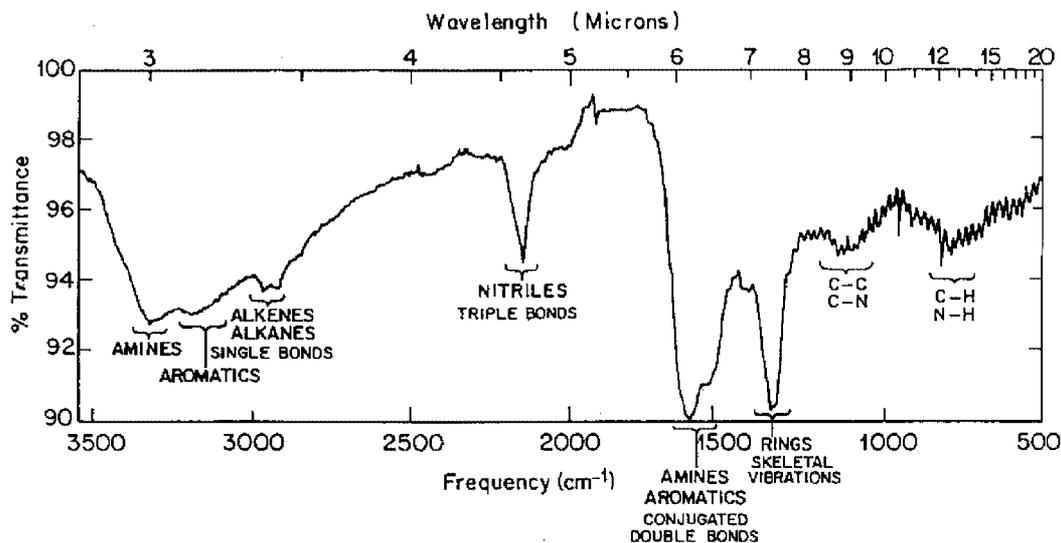
FIG. 2. The IR spectrum of solid tholin material, displaying the chemical nature of the monomer units comprising this complex polymer. Tholins appear to be a complex mixture of heterocyclic hydrocarbons, nitriles, amines, and aliphatic structures from their IR signature. Each region of this IR spectrum is a distinct spectral signature denoting a very specific bond or molecular group (see Table II and Allamandola et al. 1989).

to "skeletal ring vibrations" (after Allamandola et al. 1989) between members of C and N rings, perhaps arranged in relatively dehydrogenated, positively charged heterocyclic ring structures reminiscent of graphitic structures. The high C : H and N : H ratios of the synthesized tholin compounds and their resulting high molecular weight could also account for their tenacity when the cell was evacuated at a high vacuum pressure.

Subsequent exposure of the tholin film to atmospheric oxygen molecules and then to ambient air produced no detectable changes in the characteristic tholin spectral signature (Table I).

Introduction of air to the cell had little effect on the IR spectrum of the tholin, except to introduce a narrow, double-peaked feature around 2299–2398 cm^{-1} (4.17–4.35 μm, (reminiscent of CO_2) and to eliminate the strong aromatic feature around 3030 cm^{-1} (3 μm). The 3030-cm^{-1} feature is characteristic of the aromatic C–H stretch vibration in heterocyclic molecules (Allamandola et al. 1989). These molecules are extremely stable under radiation from UV sources, but they are especially vulnerable to oxidation. Exposure to oxygen-containing gas will decompose the hydrocarbon skeleton of the heterocyclic compound,

TABLE I

Temporal Analysis of Solid Tholin Irradiated for 60 h and Exposed to Dry Air and to Laboratory Air

Exposure time		C–H N–H	C–C C–N	Rings	Amines, aromatics	Nitriles	Alkanes, alkenes	Aromatics	Amines
	Wavelength (μm)	~11.8	~8.7	7.4	6.25	4.55	3.33	3.13	2.9
	Frequency (cm^{-1})	~850	~1150	1350	1600	2200	3000	3200	3400
Dry air									
2 min		X	X	X	X	X	X		X
18 h		X	X	X	X	X	X		X
60 h		X	X	X	X	X	X		X
Laboratory air									
0 h[a]		X	X	X	X	X	X		X
12 h		X	X	X	X	X	X		X
15 h		X	X	X	X	X	X		X
Air purged plus glow discharge									
1 cycle		X	X						
6 h[b]		X	X	X	X				
2 days[b]		X	X	X	X	X	X		

[a] As dry air result with extra double-peaked feature at 2300–2400 cm^{-1}.
[b] Appearance of a double-peaked feature at 2300–2400 cm^{-1}.

TABLE II
Temporal Analysis of Solid Tholin Synthesis in Airtight Cell

Time	C–H N–H	C–C C–N	Rings (Skeletal vibrations)	Amines, aromatics (Conjugated double bonds)	Nitriles (Triple bonds)	Alkanes, alkenes (Single bonds)	Aromatics (Double bonds)	Amines
Wavelength (μm) Frequency (cm^{-1})	~11.8 ~850	~8.7 ~1150	7.4 1350	6.25 1600	4.55 2200	3.33 3000	3.13 3200	2.9 3400
2 s			X			X	X	
10 s	X	X	X		X	X	X	
30 s	X	X	X			X		
1 h	X	X	X			X	X	
2 h	X	X	X			X	X	
3 h	X	X	X	X		X	X	
4.5 h	X		X	X		X	X	
6.5 h	X		X			X	X	
7.5 h	X	X	X			X	X	
9.5 h	X	X	X	X	X	X	X	
11.5 h	X	X	X	X	X	X	X	
13.5 h	X	X	X	X	X	X	X	
15.5 h	X	X	X	X	X	X	X	
17.5 h	X	X	X	X	X	X	X	
19.5 h	X	X	X	X	X	X	X	
23.5 h	X	X	X	X	X	X		
25.5 h	X	X	X	X	X	X		
27.5 h	X	X	X	X	X	X	X	
29.5 h	X	X	X	X	X	X	X	
31.5 h	X	X	X	X	X	X	X	X
33.5 h	X	X	X	X	X	X	X	X
35.5 h	X	X	X	X	X	X	X	
37.7 h	X	X	X	X	X	X	X	
40 h	X	X	X	X	X	X	X	X
42 h	X	X	X	X	X	X	X	X
44 h	X	X	X	X	X	X	X	X
46 h	X	X	X	X	X	X	X	
48 h	X	X	X	X	X	X	X	X
50 h	X	X	X	X	X	X	X	X
52 h	X	X	X	X	X	X	X	X
54 h	X	X	X	X	X	X	X	X
56 h	X	X	X	X	X	X	X	X
58 h	X	X	X	X	X	X	X	X
60 h	X	X	X	X	X	X	X	X

eliminating the C–H stretch signature characteristic of an intact heterocyclic molecule. The broad absorption feature around 3000 cm^{-1} in the oxygen-free tholin did not change after exposure to air. This indicates that it is exclusively due to N–H and C–H stretching vibrations, eliminating the concern that O–H contributes substantially to the IR signature of tholins exposed to air.

In addition, the presence of gas-phase acetylene around 730 cm^{-1} (13.7 μm) was confirmed, making this molecule another major product of the glow discharge of a methane–nitrogen mixture. These results are summarized in Figs. 3a and 3b and the full time-dependent inventory of products is summarized in Table II. The initial gas mixture displays a broad absorption feature characteristic of methane around 3030 cm^{-1} (~3 μm) and 1429–1250 cm^{-1}. One of the earliest features to emerge

in as little as 10 s was a very strong absorption feature around 1350 cm^{-1} (7.4 μm). This feature remains upon pumping the cell at high vacuum and appears well before the detectable C–H or N–H features are seen, indicating that a high molecular mass material of high (C + N)/H ratio may be formed almost instantaneously in these experiments. As already emphasized, the nature of this material is aromatic, consisting of hexagonal rings of carbon and nitrogen atoms and is evidence for cationic pure and nitrogenated PAHs as candidates for the fundamental building blocks of microphysical tholin particles (Bakes *et al.* 2001a,b).

To further investigate this result, the peak heights of each absorption feature were measured for all IR spectra from 2 s to 60 h, and the ratios of features arising from nitriles, amines, and "skeletal rings" relative to the methane peak (3030 cm^{-1}) were
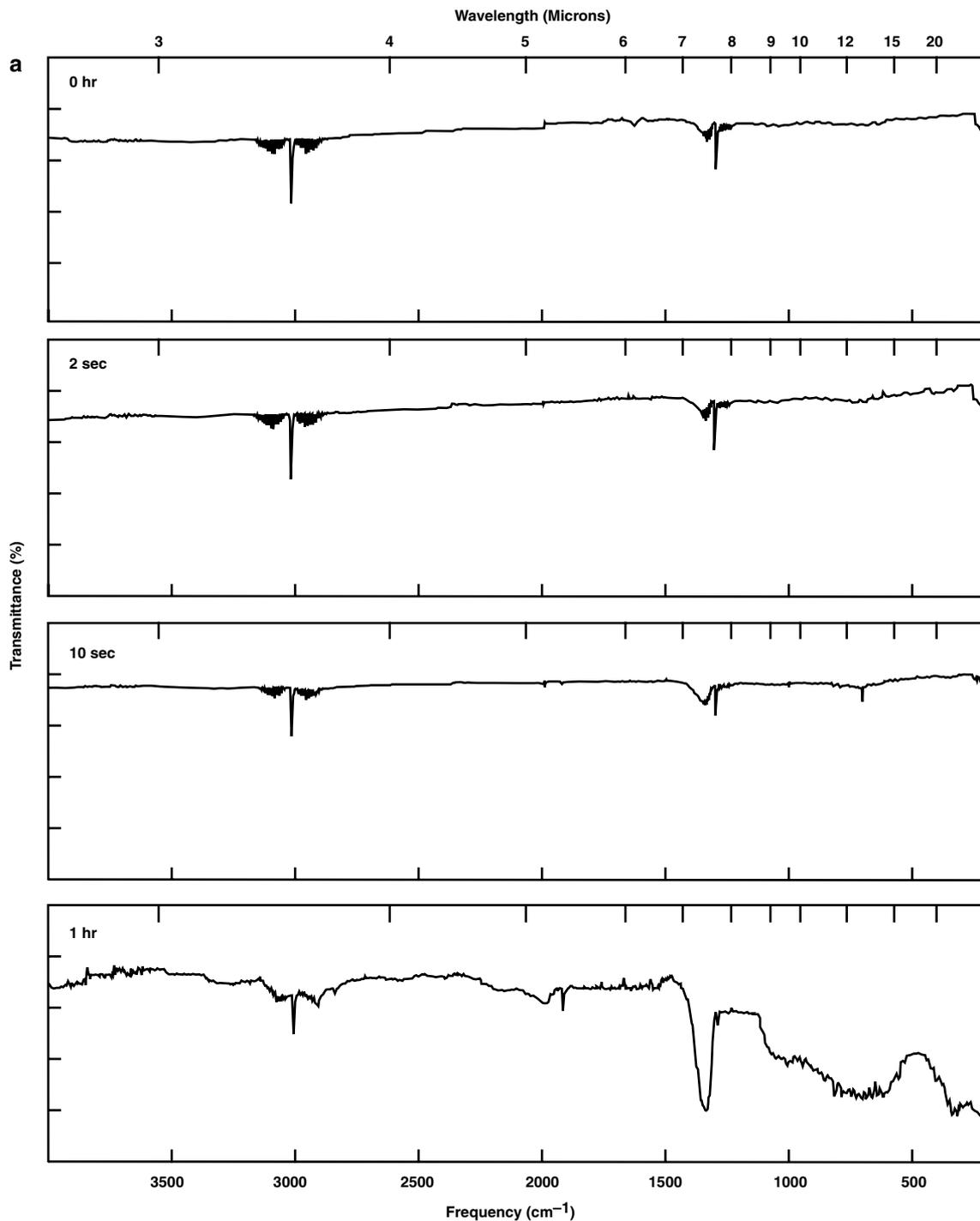
FIG. 3. (a) Time-dependent variation of the chemical composition of Titan tholin analogs from 0 to 1 h for solid- and gas-phase species. Initial signatures of aliphatic and aromatic hydrocarbons in the first 2 s are joined by spectral signatures of nitriles at 10 s. After 1 h, the nitriles have been incorporated into the tholin structure. (b) Time-dependent variation of the chemical composition of Titan tholin analogs from 2 to 60 h. The signatures of pure and nitrogenated aromatics develop and increase in intensity. After 29.5 h, the nitrile signature has returned, signaling a decrease in the saturation of the tholin compounds and general polymerization of the mixture, possibly forming HCN polymers.
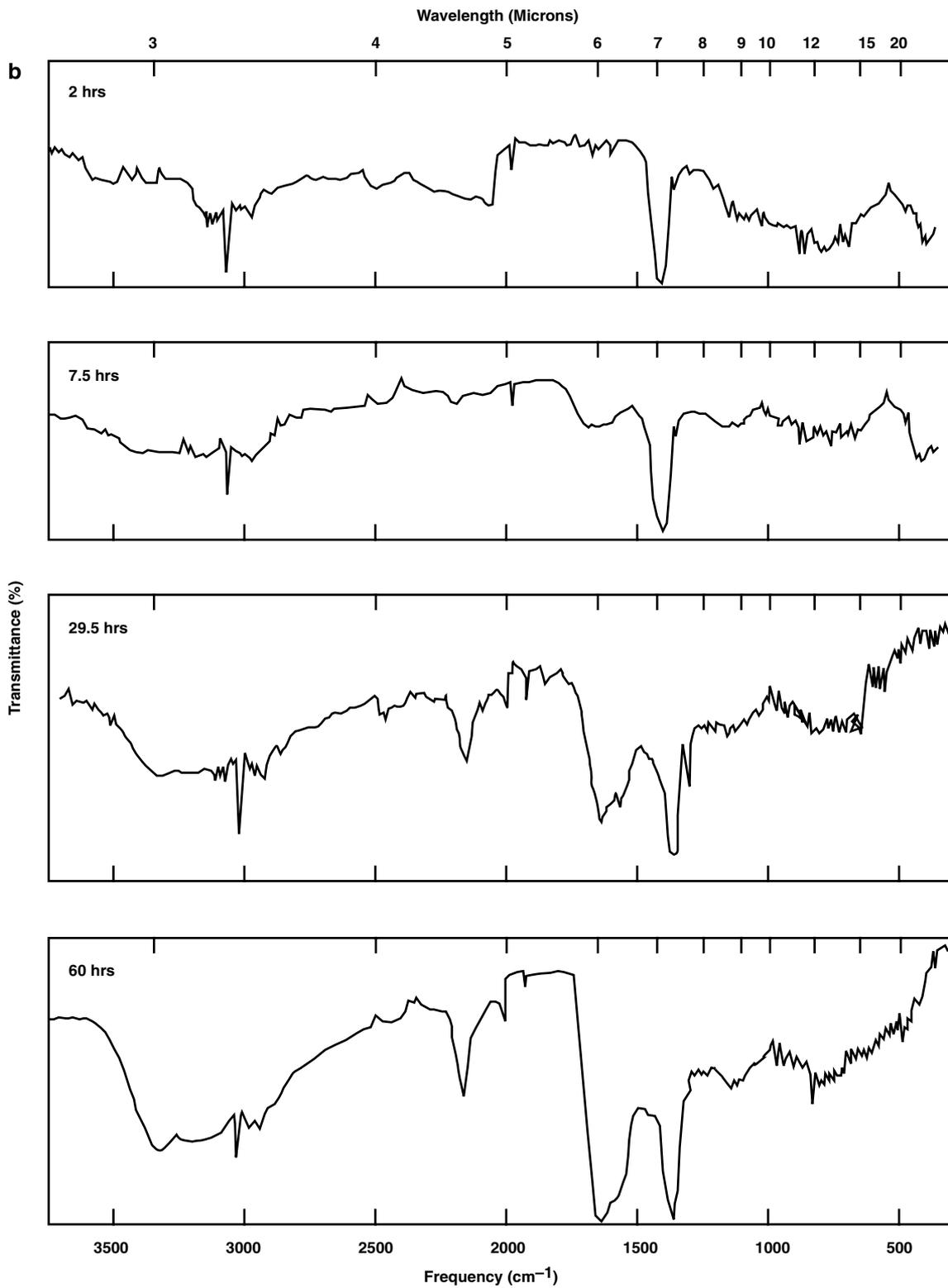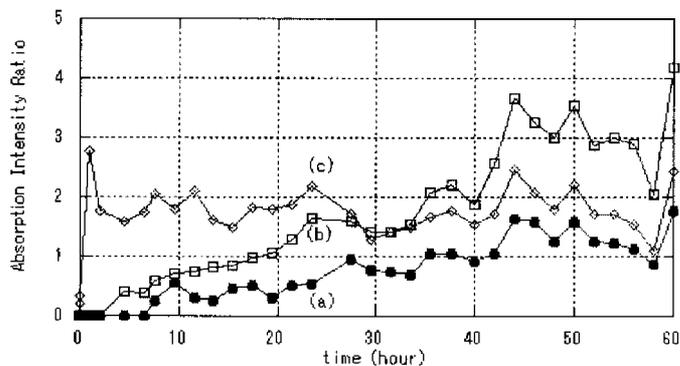
FIG. 3—*Continued*

FIG. 4. Time-dependent IR absorption intensity. The ratios of (a) nitriles (2151 cm^{-1}), (b) amines and aromatics (1600 cm^{-1}), and (c) rings (1350 cm^{-1}) to the methane (3030 cm^{-1}) absorption are plotted.

calculated. Figure 4 suggests that the aromatic ring structure is produced very quickly (within a few seconds) and remains constant. On the other hand, amines, aromatics, and nitriles seem to be produced gradually over a 10-h period. These differences in characteristic production time could be interpreted as follows. The C$_2$H radicals in the reaction vessel would be deposited to make a basic aromatic ring structure. After the base ring structure stabilizes, C$_2$H and CN radicals attach to it. This is similar to the theoretical result found by Ricca *et al.* (2001) for the quantum chemical model of the formation of nitrogenated aromatics in the Titan haze. To further elucidate the relationship between these structures and tholin polymers, more sophisticated experiments are now being conducted at NASA Ames Research Center.

5. GAS-PHASE PRODUCTS

We provide information here concerning gas-phase products as a complement to the solid-phase experiment described in this paper. The gas-phase and solid-phase experiments are two temporally separate efforts. However, the gas-phase products of tholin synthesis may strongly correlate with the chemistry of monomers and sidegroups forming the complex solid phase and give us valuable insight into the chemical processes leading to the formation of tholins from a simple CH$_4$/N$_2$ starting mixture.

Using GC/MS, Thompson *et al.* (1991) detected 59 gaseous species produced in a continuous-flow plasma discharge of 90% N$_2$ and 10% CH$_4$ at 17 mbar, but they could not detect acetylene and ammonia. Scattergood *et al.* (1989) used a variety of energy sources and detected light hydrocarbons and HCN using GC. Similarly, the pyrolytic products of a tholin usually determined by GC/MS also add information about the breakdown components of a tholin's structure (Jupiter: Khare *et al.* (1982), Titan: Table 2 in Sagan and Thompson (1984)). Both sets of information are of immense importance for tholins because they are not simple polymers. We have exploited both methods to learn about the composition of the structure of Titan tholin (Khare *et al.* 1984b, Thompson *et al.* 1991). We have analyzed the unpublished IR spectra of the gas-phase products that were

measured by Sagan and Thompson (1984) and are presenting the results for the first time. The experimental conditions of Sagan and Thompson's (1984) work were not exactly the same as ours. However, their results will be useful in understanding the chemical processes occurring during the formation of tholins.

5.1. Experimental Objectives

Gas-phase products in any simulation experiments where tholins are produced help us to understand possible functional groups in the tholin. Gas-phase products are the precursor to the formation of tholins and any information about their identity is useful. Our experimental objective is to use the IR spectra of gas-phase species to identify possible monomer units and functional groups of complex tholin polymer.

5.2. Experimental Method

A mixture of 9% CH$_4$ and 91% N$_2$ was exposed for $\sim$10^7 s at a total pressure of 73 mbar and room temperature to a high-frequency electrical discharge corresponding approximately to 50-keV electrons. A thin, red tholin film gradually built up in the reaction vessel. Scanning electron microscopy revealed a particle size distribution function peaking between 0.1 and 0.5 μm, with occasional irregular large particles present to tens of micrometers.

The total volume of the reaction vessel was 14,510 cm^3. It contained 97 cm^3 CH$_4$ and 951 cm^3 N$_2$. The amount of gas after the experiment was 996 cm^3. Since the amount of gas before the experiment was 1048 cm^3, the decrease in the amount of gas was 52 cm^3. By using liquid helium to condense all the gases at the end of the experiment and then raising the temperature to that of liquid nitrogen, the amount of gas that is noncondensable at 77 K was calculated to be 831 cm^3 and the amount of condensable gas was calculated to be 165 cm^3. The amount of Titan tholin from the walls of the reaction vessel was measured by filling the reaction vessel with spectrograde acetonitrile, subjecting the vessel to ultrasonic vibrations to remove the tholins from the walls of the reaction vessel, and then removing the solvents by evaporation. The total amount of Titan tholin obtained was 70.25 mg.

6. RESULTS AND DISCUSSION FOR GAS-PHASE PRODUCTS

The gas-phase IR spectrum of the condensable gases at 77 K is shown in Fig. 5. This spectrum clearly shows the synthesis of ammonia as all the ammonia bands at 1628, 3414, 968, 932, and 3337 cm^{-1} are present (Herzberg 1960, Chapter 1 and 2). Some CH$_4$ also condensed along with other species as we find CH$_4$ bands at 3020 and 1306 cm^{-1}. The synthesis of acetylene C$_2$H$_2$ in this experiment is interesting as this molecule is known to lead to the formation of aromatic molecules such as benzene, which, in an atmosphere of ionized nitrogen around the spark discharge region between the electrodes, can lead to the formation of nitrogenated aromatic compounds. This yields evidence of acetylene
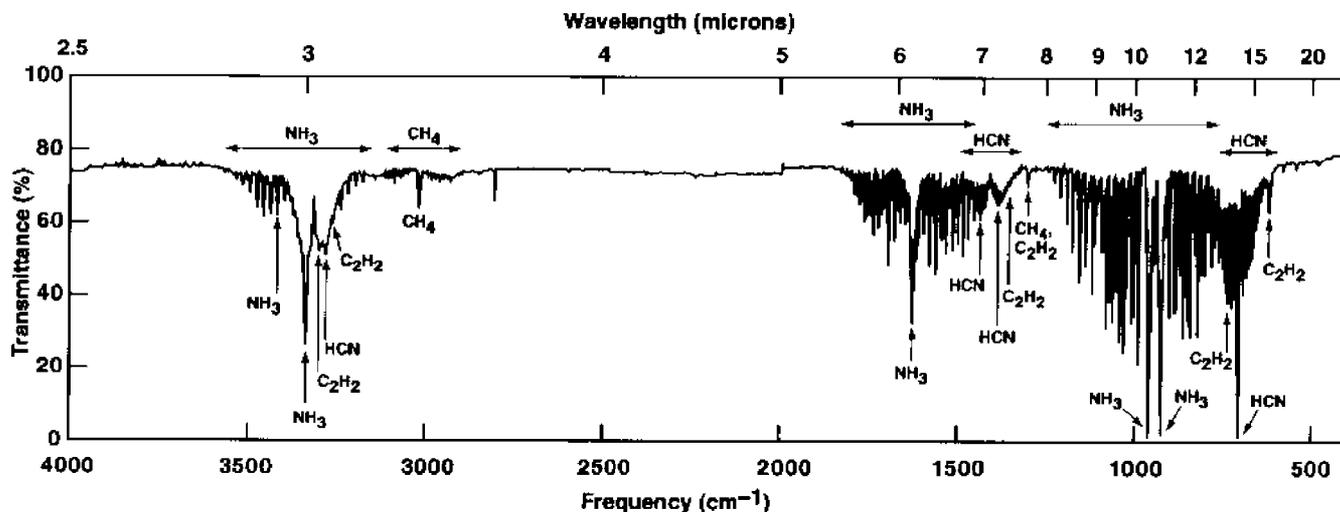
FIG. 5. The gas-phase products for Titan tholin analog synthesis. These simple molecules, which are breakdown products of the initial CH_4/N_2 mixture, are composed generally of hydrocarbons and nitrogen-containing species. They may be polymerized into solid tholin under the glow discharge mechanism described in this paper. The gas phase displays a rich chemistry with varied building blocks for Titan tholin analogs.

formation via its characteristic IR spectral signatures around 730, 1306, 1356, 3260, and 3306 cm^{-1}, present in the overall spectrum of the condensable gases. However, the strongest band of acetylene at 730 cm^{-1} is superimposed onto the strongest band of HCN at 709 cm^{-1} and the second strongest band of acetylene at 1306 cm^{-1} is superimposed onto the methane band at 1306 cm^{-1}. The acetylene band at 1356 cm^{-1} is at the shoulder of the HCN band at 1379 cm^{-1}, while both the bands of acetylene at 3260 and 3306 cm^{-1} are superimposed with the ammonia band at 3337 cm^{-1}. After ammonia, the next most abundant product in the spectrum in Fig. 5 appears to be hydrogen cyanide, with bands at 709, 1439, 1379, and 3279 cm^{-1}. Since IR spectroscopy is not a very sensitive technique for the identification of the minor constituents in a gas mixture and since there was no attempt to separate the gas components prior to analysis, identification of the components in the condensed gases at 77 K after the end of the experiment was limited only to CH_4, NH_3, HCN, and C_2H_2. Gupta *et al.* (1981) have performed a similar experiment in which they identified HCN and C_2H_2 as the primary products via IR spectroscopy. The other products that they identified by GC and GC/MS in order of decreasing abundance were C_2H_4, C_2H_6, C_4H_2, C_3HN, and C_3H_6. Two additional compounds, C_3H_8 and CH_3CN, were found in trace quantities. Scattergood *et al.* (1989) have also studied the Titan atmosphere by laser-induced plasma methods and have reported synthesis of similar species in the gas-phase and the formation of tholins on the walls of the reaction vessel. The most detailed study of 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 of 17 and 0.25 mbar were undertaken by Thompson *et al.* (1991), who used the results to compute expected abundances of minor constituents in Titan's atmosphere. In recent work on

the simulation of Titan's atmosphere Ramirez *et al.* (2001) have also detected small, unsaturated hydrocarbons, nitriles (including HCN), and aromatic compounds by GC/MS–FTIR from a mixture of 10% CH_4 in N_2 subjected to irradiation with a variety of energy sources.

The detection of HCN and C_2H_2 as gaseous products in the gas-phase experiment is important, since during prolonged discharge, they can participate in the production of nitrogenated aromatic compounds as part of a tholin structure. In fact, the pyrolysis GC/MS analysis of Titan tholin not only produces saturated and unsaturated aliphatic hydrocarbons but substituted polycyclic aromatics, nitriles, amines, pyrroles, pyrazines, pyridines, pyrimidines, and the purine, adenine (Khare *et al.* 1984b). Two-step laser desorption/multiphoton ionization mass spectrometry reveals a range of two- to four-ring PAHs, some with one to four alkylation sites, with net abundance of 10^{-4} g g^{-1} of tholins produced. Synchronous fluorescence techniques have confirmed this detection (Khare *et al.* 2001). Titan tholin has more one- and two-ring PAHs than four-ring and larger PAHs. Solid state ^{13}C NMR spectroscopy suggests that 25% of the total carbon in the tholin is tied up in aromatic and/or aliphatic alkenes. IR spectra of the Titan tholin indicate an upper limit of 6% by mass in benzenes, heterocyclics, and PAHs with more than four rings. As with interstellar PAHs, the synthesis route of planetary PAHs is likely to be via acetylene addition reactions (Sagan *et al.* 1993, Bauschlicher and Ricca 2000, Ricca *et al.* 2001).

7. CONCLUSIONS

Titan's haze dominates its temperature, atmospheric circulation, and climate control because the haze particles exert a significant influence over the thermodynamics and radiation

absorption properties of the atmosphere, as well as its complex organic chemistry. Characterization of both the molecular and the submicrometer components of the haze is therefore vital for understanding the global properties of Titan. In this investigation, we discuss synthesized Titan tholin analogs and the results of a time-dependent analysis of both the solid- and gas-phase products of a mixture of 90 mol% N_2 and 10 mol% CH_4 subjected to an inductive glow discharge. The total time of discharge and refill (to simulate inflow from the CH_4/N_2 reservoir in Titan's upper atmosphere) was 60 h, followed by exposure to both dry and laboratory air, respectively, to observe potential oxidation products (dry air) and the effects of H_2O (laboratory air). Our Titan haze synthesis produced a wealth of organic molecules, including alkanes, alkenes, aromatic ring hydrocarbons, nitriles, amines, and various sidegroups such as C–H and N–H. We believe that these structures are the intermediates in the aerosol structure between simple hydrocarbons a few Ångstroms in size and microphysical tholin particles of radius a few micrometers. For the IR spectra of the solid tholin material, the O_2-free situation is consistent with spectra taken after exposure to air. The replenishment process yields a product similar to that of material for which optical constants have been measured (Khare *et al.* 1984a). The rapid appearance of a tenacious feature at 1350 cm^{-1} can be assigned to skeletal ring vibrations between members of nitrogen-containing aromatic rings of a high molecular weight product comprised of carbon rings with a low abundance of H attached to the component carbon atoms. The detection of acetylene and hydrogen cyanide as the major products reported in the gas-phase experiment may strengthen our theoretical models for the formation of aromatic molecules in the Titan haze. The presence of aromatics in Titan tholin is confirmed after subjecting tholins to rigorous analytic techniques during this experiment. While previous research by McKay (1996) and Clarke and Ferris (1997a,b) initiated preliminary studies of chemical evolution in the Titan haze under a variety of conditions, future Titan haze tholin analog experiments should investigate a range of temperatures, pressures, energetic charged particles, and UV fluxes appropriate to Titan. In addition, the nature of the starting mixtures should be varied such that instead of starting off with CH_4 and N_2, we use C_2H_2, HCN, C_6H_6, and related compounds such as C_6H_5N and HC_3N. An understanding of the chemical nature of the building blocks of tholins will shed light on the global properties of the Titan haze and guide exploratory missions into the Titan haze such as the Cassini Huygens probe as it explores and measures the atmospheric composition (McKay *et al.* 2001).

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