Chemical composition of Titan's haze: Are PAHs present?

Melissa G. Trainer,[1] Alexander A. Pavlov,[2] Jose L. Jimenez,[1] Christopher P. McKay,[3] Douglas R. Worsnop,[4] Owen B. Toon,[2,5] and Margaret A. Tolbert[1]

[1] Previous laboratory studies of haze aerosols analogous to those in Titan's atmosphere have shown evidence of the formation of polycyclic aromatic hydrocarbons (PAHs). If present, PAHs may provide a mechanism for both particle formation and nitrogen incorporation. We have conducted new experiments simulating Titan haze production using an Aerosol Mass Spectrometer (AMS). The AMS allows us to examine the chemical structure of the haze particles under a variety of starting conditions in real-time and without collection. Our results for particles produced from a mixture of 10% CH_4 in N_2 are consistent with a large fraction of aromatics, including specific m/z peaks likely due to PAHs. However, at lower concentrations of CH_4 (1% and lower), the mass fraction of PAHs greatly diminishes, and an aliphatic pathway dominates. Haze containing sediments may trace the history of methane on Titan through their composition. The implications for Titan haze and for observations from the Huygens probe are discussed.   INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0343 Atmospheric Composition and Structure: Planetary atmospheres (5405, 5407, 5409, 5704, 5705, 5707); 5405 Planetology: Solid Surface Planets: Atmospheres— composition and chemistry; 6280 Planetology: Solar System Objects: Saturnian satellites. Citation: Trainer, M. G., A. A. Pavlov, J. L. Jimenez, C. P. McKay, D. R. Worsnop, O. B. Toon, and M. A. Tolbert (2004), Chemical composition of Titan's haze: Are PAHs present?, Geophys. Res. Lett., 31, L17S08, doi:10.1029/2004GL019859.

1. Introduction

[2] Haze aerosols produced in the laboratory from simulated Titan atmospheres provide an excellent match with the optical properties of Titan's haze [Khare et al., 1984]. The chemical structure of the haze may be a key to understanding the complex chemistry of Titan's atmosphere. While the gas-phase chemistry of Titan's atmosphere has been extensively modeled, there remains a gap in understanding the processes linking these gaseous precursors to the formation of haze particles [Toublanc et al., 1995; Yung et al., 1984]. Hydrocarbons including C_2H_2, C_2H_4, C_2H_6, C_3H_8, etc. have been observed in Titan's atmosphere spectroscopically [Coustenis et al., 2002], and have also been detected as the products of methane chemistry in Jupiter's atmosphere [Wong, 2001]. These molecules serve as the preliminary building blocks of several mechanisms that predict chemical reaction pathways for particle formation. Some of the mechanisms that have been proposed include haze formation pathways through the polymerization of acetylene [Allen et al., 1980; Lebonnois et al., 2002; Wilson and Atreya, 2003], the production of PAHs [Friedson et al., 2002; Lebonnois et al., 2002; Wilson and Atreya, 2003; Wong et al., 2000], and the formation of nitriles [Lebonnois et al., 2002; Wilson and Atreya, 2003]. Results from several of these studies indicate that the formation of aromatics may be the most likely explanation for particle production. Further, a computational study by Ricca et al. [2001] provides a mechanism which demonstrates that the inclusion of nitrogen into the PAHs may enhance the production and stabilization of these molecules. Definitive characterization of the chemical composition of the haze particles produced in the laboratory is needed to help constrain the models. Early laboratory studies of Titan haze formation reported the appearance of aromatic molecules, although upper limits were placed on their expected concentrations [Sagan et al., 1993]. More recent results by Khare et al. [2002] show that during laboratory simulations of haze production, aromatic ring structures are formed rapidly and remain prevalent during particle formation.

[3] One complication in discussing Titan haze is the possibility that the haze formation mechanism may not be consistent throughout Titan's atmosphere [Chassefiere and Cabane, 1995]. It may be affected by the concentration of certain constituents, local pressure, temperature, and radiation and energy source. While a host of laboratory experiments probing the chemical composition of the haze aerosols have focused on many of these parameters [McKay et al., 2001], the effect of atmospheric CH_4 concentration on particle composition has not been explored. Rather, the majority of laboratory studies of Titan haze analogs have used a standard mixture of 10% CH_4 in N_2 as the approximation of Titan's atmosphere. Other studies have focused on the photochemical reactions of CH_4 without N_2 present [Adamkovics and Boering, 2003]. The concentration of CH_4 in the stratosphere of Titan has been estimated to be between $1-5\%$ [Lellouch et al., 1989]. Here we discuss laboratory results that suggest the relative concentration of CH_4 in N_2 appears to affect the chemical composition of the atmospheric haze, and therefore the reaction pathways of particle formation.

[1]Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder, Boulder, Colorado, USA.
[2]Laboratory for Atmospheric and Space Physics, University of Colorado at Boulder, Boulder, Colorado, USA.
[3]Space Science Division, NASA Ames Research Center, Moffett Field, California, USA.
[4]Aerodyne Research Incorporated, Billerica, Massachusetts, USA.
[5]Also at Program in Atmospheric and Oceanic Sciences, University of Colorado at Boulder, Boulder, Colorado, USA.

2. Experimental Methods

[4] A flow system [*Clarke et al.*, 2000] was designed to produce Titan-like haze aerosols using a range of starting CH_4 concentrations. For each starting condition, the particles' chemical composition was determined in real-time using an AMS [*Jayne et al.*, 2000]. In the flow system, CH_4 was introduced into the mixing chamber at pressures from 15.6 to 1000 Torr as measured by an MKS Baratron Model 626A capacitance manometer. The mixing chamber was then pressurized with N_2 to allow for final mixing ratios of CH_4 in N_2 of $0.1-10\%$ as monitored with a regulator gauge with absolute pressures in the range of $7800-20,800$ Torr. Sufficient mixing time was allowed to ensure complete mixing of the gaseous species in the chamber [*Clarke et al.*, 2000]. After mixing, the gas was continuously flowed through the reaction cell using a Mykrolis FC-2900 Mass Flow Controller ($0-100$ standard $cm^3 min^{-1}$ capacity), providing control over the operating pressure and flow rate in the reaction cell. The reaction pressure was held at 600 Torr, to allow for both proper instrument function and to ensure sufficient signal for analysis. The haze particles were formed in the reaction cell using an electrical discharge created by a Tesla coil applied to electrodes in the reaction cell. The output of the reaction chamber (with haze particles) was flowed into the AMS.

[5] An electrical discharge source was used in these experiments in order to break the N_2 bonds desired for the incorporation of N-atoms into the haze material. The comparison of multiple data sets of laboratory-produced haze has shown that the optical properties of the aerosols that include N provide a much better match to the optical constants of Titan than haze material produced in the absence of N_2 [*McKay et al.*, 2001; *Sagan et al.*, 1992]. Other laboratory results indicate that the color of the haze material is regulated by nitrogen incorporation [*McKay*, 1996].

[6] The AMS, developed and built by Aerodyne Research [*Jayne et al.*, 2000], can obtain quantitative data without exposing aerosols to laboratory air, providing averaged mass spectra of the bulk non-refractory aerosol. The instrument employs a particle-focusing lens to direct the aerosols onto a heated surface where they are flash vaporized under high vacuum ($\sim 10^{-8}$ Torr) and ionized using electron impact ionization. A quadrupole mass spectrometer (QMA 410, Balzers, Liechtenstein) is used to obtain mass spectra. Instrument design, modes of operation, and data analysis techniques are described by *Allan et al.* [2003], *Jimenez et al.* [2003], and *Jayne et al.* [2000]. In this study the vaporization temperature was $600°C$, and the electron energy was 70 eV.

3. Results and Discussion

[7] Mass spectra for particles produced in mixtures of 10, 3, 1, 0.3 and 0.1% CH_4 in N_2 are shown in Figure 1. The concentrations encompass the upper and lower limits of the volume mixing ratio of CH_4 on Titan. The mass spectrum given for 10% CH_4 (Figure 1a) contains a variety of mass peaks which appear to originate from aromatic species. The identification and analysis of mass spectral peaks, as well as relevance to predicted chemical pathways, are included in Table 1. Standards analyzed in the AMS confirm the
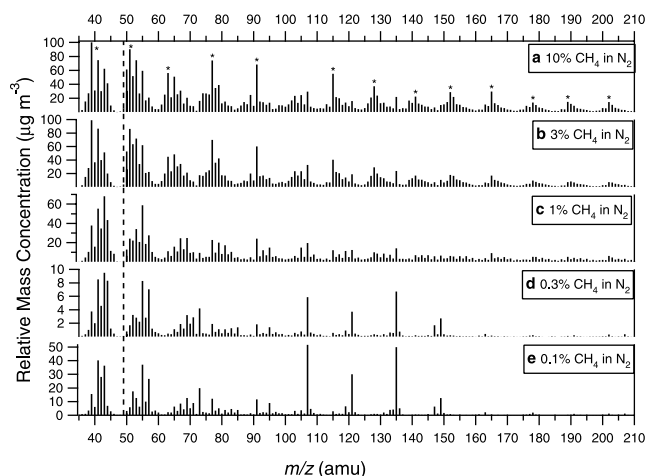

Figure 1. Representative AMS mass spectra for haze aerosols produced in various concentrations of CH_4 in N_2 at 600 Torr. The data shown to the right of the dashed line at 49 amu have been multiplied by two for ease of viewing. The mass concentrations for all spectra have been multiplied by a scaling factor of 3.2, so that the 10% CH_4 spectrum has a maximum peak value of 100. The asterisk mark peaks identified as PAH fragments and listed in Table 1.

assignment of a few of these peaks as PAHs. This series of aromatic mass peaks is similar in the 10 and 3% CH_4 mass spectra (Figures 1a and 1b), but its intensity decreases in the 1% CH_4 mass spectrum (Figure 1c) and these m/z's do not show significant signal in the 0.3 and 0.1% CH_4 mass spectra (Figures 1d and 1e). As the aromatic signal decreases a new set of mass peaks grows in importance, as can be seen in the aerosol mass spectrum for 0.3 and 0.1% CH_4 in N_2. Additional studies of CH_4 in argon which also show the appearance of these peaks at low CH_4 concentrations show that they are not nitrogen-containing species. Further, we are confident that these peaks are not an experimental artifact as they do not appear when the Tesla coil is off or when the particles are filtered. Comparisons of the spectra shown in Figures 1d and 1e to the NIST standard library of mass spectra find that these mass peaks show the best agreement with the spectra of various terpene molecules and other similarly structured alkenes. We feel that this indicates that the particles formed in low CH_4 concentrations are comprised of aliphatic organic species, which are more saturated than aromatics and contain non-conjugated double bonds. These data thus imply that as the relative concentration of CH_4 in N_2 is decreased there is a transition between a production pathway that generates aromatic species to one which produces aliphatic species. This figure also shows that the relative aerosol mass that is produced decreases with decreasing CH_4, although much less than linearly.

[8] The transition between the two pathways is further illustrated in Figure 2. Here select aromatic and aliphatic peak intensities are plotted as a function of CH_4 concentration. The mass peak at m/z 51 is a large fragment peak that, while present in all of the aerosol mass spectra (Figure 1), is only dominant in spectra where aromatics are present. Likewise, the mass peak at m/z 115 is also an aromatic indicator seen in these spectra. We use the ratios of m/z 51

Table 1. Chemical Family Assignments to Peaks in Mass Spectra (Figure 1) and Relation to Predicted Chemical Pathways

Chemical Family[a] (and Main Fragments)	Peaks in Mass Spectrum	CH_4 Concentrations Where Peaks are Dominant	Models Predicting Presence of Chemical Family
PAHs ($C_6H_5^+$, $C_{10}H_8^+$, $C_{14}H_{10}^+$, etc.)	39, 51, 63, 77, 115, 128, 152, 165, 178, 189, 202[b]	10, 3, 1	*Wong et al.*, 2000 (Jupiter) *Friedson et al.*, 2002 (Jupiter) *Wilson and Atreya*, 2003 (Titan)
Alkylated PAHs (C_6H_5-$C_nH_{2n}^+$, $C_{10}H_7$-$C_nH_{2n}^+$, etc.)	91, 105, 119... 142, 156, 170...	10, 3, 1	
Nitrile (HCN^+)	27 (not shown in Figure 1)	all concentrations	*Lebonnois et al.*, 2002 (Titan) *Wilson and Atreya* 2003 (Titan)
Terpene-like aliphatic ($C_8H_{11}^+$, $C_9H_{13}^+$, $C_{10}H_{15}^+$)	107, 121, 135	0.3, 0.1	
Polyacetylene	no evidence from data	none	*Allen et al.*, 1980 (Titan) *Lebonnois et al.*, 2002 (Titan)

[a]Peak assignments made using various resources [*Hankin and John*, 1999; *McLafferty and Venkatararghavan*, 1982; *McLafferty and Turecek*, 1993].
[b]Peaks listed are shown with asterisks in Figure 1a.

to the total mass signal and of *m/z* 115 to the total mass signal in each spectrum as indicators of the production of aromatic species. Likewise, we use the ratios of *m/z* 107 to the total mass signal and of 135 to total mass signal as markers for the aliphatic series. The evolution of these peaks as a function of CH_4 concentration in N_2 shows the transition between the two pathways occurring when the CH_4 concentration is at approximately 1%.

[9] In order to probe the inclusion of nitrogen into the haze material, we repeated the above experiments using argon (Ar) as the background gas instead of N_2. The most prominent difference we note between the two sets of experiments is the intensity of *m/z* 27. The peak at *m/z* 27 is the largest product peak in the mass spectra of aerosols produced in N_2, but is a minor product in the Ar aerosols. The mass peak at *m/z* 27 in the particle mass spectra has contributions both from hydrocarbon fragments ($C_2H_3^+$) and from nitrile compounds (HCN^+). It should be noted that these ions represent fragments of larger molecules within the aerosols produced, and do not represent gas phase species such as HCN since the AMS discriminates against gases by a factor of $\sim 10^7$ as compared to the particles. We used the mass peaks in the series *m/z* 27, 41, and 55 in the spectra from particles produced in Ar to estimate the hydrocarbon contribution to the *m/z* 27 peak in the N_2 data. This contribution is subtracted to obtain an approximate value for the HCN^+ fragment ion. A ratio of this value to the total aerosol mass in each spectrum yields a consistent percentage of HCN^+ in the aerosol molecules of approximately 13.9 ± 0.03% by mass, independent of $[CH_4]$ from 0.1 to 10% CH_4. This gives us a lower limit for the mass percent of nitrogen in the haze particles of about 7%. For comparison, other studies using the Tesla coil discharge have reported an elemental ratio of approximately $C_{11}H_{11}N_2$ in the Titan haze aerosols, which is a nitrogen incorporation of approximately 16% by mass [*McKay*, 1996]. Our estimation provides a reasonable lower limit, which implies that there is a considerable amount of nitrogen incorporation into the haze aerosols.

4. Implications for Titan Haze and the Huygens Probe

[10] In our experimental study simulating Titan haze formation, we have shown that as the CH_4 concentration in N_2 varies we can distinguish different chemical pathways

for aerosol production. At higher concentrations of CH_4, our spectra are consistent with the formation of PAHs and aromatics. At the lower CH_4 concentrations (<1%), we see instead the formation of particles from predominantly aliphatic molecules that have a distinct chemical composition from those formed in the higher CH_4 concentrations. This compositional dependence on methane mixing ratio may have implications for aerosol formation in Titan's atmosphere across regions or times in which the concentration of CH_4 may vary. If there are no exposed sources of CH_4 at Titan's surface, the CH_4 concentration must fall over time as methane is converted into larger hydrocarbons. Hence Titan haze aerosols may be evolving from one chemical regime toward another. If there are intermittent sources at the surface, then the composition may vary in a more complex manner over time. Hence, the composition of the haze accumulated on the surface of the moon may provide a stratigraphic record of the changing CH_4 abundance in the atmosphere. If there are CH_4 gradients in the photochemical region of Titan's atmosphere, then different classes of haze aerosols may be produced. The chemical composition of the hazes may vary spatially with atmospheric CH_4 concentration, and the optical properties would probably vary as well. The different classes of haze aerosol may help to explain the seasonal albedo changes that have been observed for Titan [*Lorenz et al.*, 2001].
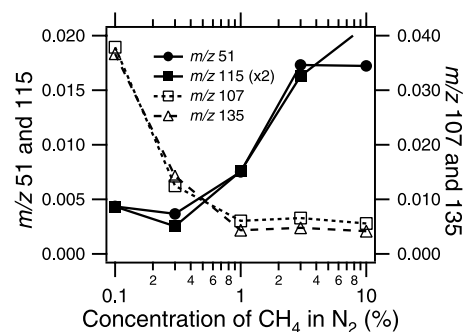

Figure 2. Ratios of several mass peaks to the total mass in the particle mass spectra, taken from data shown in Figure 1. Mass peaks *m/z* 51 and 115 were chosen to represent the aromatic mass fragments and the mass peaks *m/z* 107 and 135 represent the aliphatic hydrocarbons.

[11] Based on our results, we suggest the Huygens Probe may find that there is a correlation between the chemical composition of the haze and the atmospheric CH_4 composition. The Aerosol Collector Pyrolyser (ACP) [*Israel et al.*, 2002] and Gas Chromatograph Mass Spectrometer (GCMS) [*Niemann et al.*, 2002] will measure both of these parameters during its descent through Titan's atmosphere. However, the sampling of the ACP coupled with the GCMS within the stratosphere will occur at approximately 130 km, well below the main haze formation region around 300–500 km [*McKay et al.*, 2001]. The highest altitude gas composition measurements taken by the GCMS will occur at approximately 170 km in Titan's atmosphere, also below the main formation region. Therefore, the measurements taken by these instruments may not directly illuminate the connection we are proposing between atmospheric CH_4 concentration and haze composition. However, it is possible that the ACP/GCMS may observe different chemical compositions from its two sampling regions. It should be noted that the ACP/GCMS will not be able to directly identify high molecular weight PAHs due to decomposition within the pyrolyser, but would instead observe a large signal for benzene if PAHs are present [*Israel et al.*, 2002]. Because PAH presence would be an important clue for the significance of the high CH_4 pathway of particle formation, such a determination may be important to understanding the aerosol composition on Titan.

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J. L. Jimenez, M. A. Tolbert, and M. G. Trainer, Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder, Campus Box 216, Room 318, Boulder, CO 80309-0216, USA. (tolbert@spot. colorado.edu)

C. P. McKay, Space Science Division, NASA Ames Research Center, Moffett Field, CA, USA.

A. A. Pavlov and O. B. Toon, Laboratory for Atmospheric and Space Physics, University of Colorado at Boulder, Boulder, CO 80309, USA.

D. R. Worsnop, Aerodyne Research Incorporated, Billerica, MA, USA.