



Chemical composition of simulated Titan's midatmospheric aerosols

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[1] A large fraction of the major unsaturated species (C_2H_2 , C_2H_4 , HCN, and HC_3N) with mixing ratios of about 3×10^{-6} , 10^{-7} – 10^{-8} , 3×10^{-7} , and 10^{-9} – 10^{-10} reside in Titan's atmosphere between 150 and 500 km (Vinatier et al., 2009; Coustenis et al., 2007) before they condense near the tropopause. A large flux of medium-wavelength UV penetrates down to these levels, resulting in the polymerization of these unsaturated compounds and the formation of aerosols. We performed our experiments on aerosol formation at these altitudes where both abundances and solar UV flux are high, bearing in mind that additional photolysis occurs at both higher and lower altitudes. In the gas phase, C_2H_2 photolysis results in unsaturated C_4 species that, on further addition of C_2 , form the cyclic benzene. These gas-phase intermediates are consumed when an acetylene-poor gas mixture is irradiated for a long time, giving rise to larger solid-state species, mainly by addition of C_2 , followed by further cyclization. The largest species formed was the condensed 5-ring benzopyrene, not the 7-ring coronen molecule, which could have been detected there. Another fraction of the polymers consists of polyvinyl and vinyl acetylene chains, which are cross-linked due to their labile π electrons and form an insoluble solid matrix. This explains the reduction of the C:H ratio from the condensed aromatics of 1.2 to the measured C:H = 1.013 ± 0.001 of the polymers.

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1. Introduction

[2] After many years of very prolific remote sensing, which revealed to us the molecular composition of Titan's atmosphere [e.g., Coustenis et al., 2003; Hanel et al., 1981; Maguire et al., 1981; Kunde et al., 1981], we have in situ measurements of the chemical species present at various altitudes: Niemann et al. [2005] measured, using the Huygens gas chromatograph-mass spectrometer (GC-MS), the major atmospheric components at 132–120 km and on the surface. Waite et al. [2005] made measurements using Cassini's Ion Neutral Mass-Spectrometer (INMS) and in 2007 added measurements by Cassini's Plasma Spectrometer (CAPS), Electron Spectrometer (ELS) and Ion Beam Spectrometer (IBS) to the atmospheric composition around 1000 km. Niemann et al. [2005] and Waite et al.'s [2005, 2007] measurements are invaluable for the understanding of Titan's complex chemistry. At ~1000 km Waite et al. [2007] measured by the INMS a plethora of small species, such as C_2H_2 , C_2H_4 , and HCN that are produced from CH_4 and N_2 , and many others that arise from the C_2 species and HCN, such as C_3H_4 , C_3H_6 , HC_2N , C_4H_2 , C_2N_2 , HC_3N , H_3C_4N , and C_6H_6 (benzene) as major species. The CAPS and IBS

analyzer identified in the positive ion spectrum naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$). The negative ion spectrum showed a large number of masses up to 1200 amu, which decreases to a 10^{-4} smaller abundance at 40,000 amu. The large abundances of positive ions observed by Waite et al. [2007] at 1000 km suggested to them that at this altitude ion-molecule reactions are producing more complex hydrocarbon molecules, from benzene to PAHs.

[3] The Cassini/Composit InfraRed Spectrometer (CIRS) measured the minor atmospheric species at lower altitudes, between ~450 and ~150 km [Vinatier et al., 2009; Coustenis et al., 2007]. The mixing ratios of the unsaturated, polymerizable, species C_2H_2 , C_2H_4 , HCN, HC_3N were found to be about 3×10^{-6} , 10^{-7} – 10^{-8} , 3×10^{-7} , and 10^{-9} – 10^{-10} respectively. Due to the ~20 km scale height, these species are more abundant at 450–150 km compared with 1000 km. Moreover, C_2H_6 liquefies in the tropopause but passed this cold barrier and was detected on the surface by the GC-MS on board the Huygens probe [Niemann et al., 2005]. It is also a component of the lakes [Brown et al., 2008].

[4] Although high-energy particles are essential for breaking the strong N_2 bond and producing nitriles, solar UV radiation is still the major energy source in Titan's atmosphere [Sagan and Thompson, 1984; Galand et al., 1999; Keller et al., 1992; Stevens, 2001; Tran et al., 2005]. The solar UV flux capable of photolyzing CH_4 at $\lambda < 1440$ Å and produce C_2H_2 is $10.58 \times 10^{-3} \text{ W m}^{-2}$ [Thekaekara, 1976; Ackerman, 1971] about 10 times larger than the Saturnian

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magnetospheric particles flux ($1.1 \times 10^{-3} \text{ W m}^{-2}$), solar wind particles flux ($0.23 \times 10^{-3} \text{ W m}^{-2}$), and the flux of cosmic rays ($1.16 \times 10^{-3} \text{ W m}^{-2}$) [Dimitrov and Bar-Nun, 2004]. Lightning and its subsequent thunder shock waves could convert CH_4 to C_2H_2 [Bar-Nun, 1975]. However, according to the Huygens Atmospheric Structure Instrument (HASI) findings [Fulchignoni et al., 2005], lightning activity on Titan is very scarce, if not absent altogether. Fischer et al. [2007] reported the nondetection of radio emission from lightning by the Cassini RPWS instrument after 36 Titan flybys. This can be expected from the absence of a heat source to drive charge separation in Titan's quiescent and nonpolar molecular atmosphere [Desch et al., 2002]. However, Morente et al. [2008] suggested recently that they could extract from the HASI-Huygens data faint Schumann Resonances from Titanian lightning discharges. Whether these faint signals are significant has still to be ascertained.

[5] The solar UV flux capable of photolyzing the unsaturated C_2H_2 , C_2H_4 , HCN, and HC_3N and their subsequent photoproducts, between 1440 and 4000 Å is significant: 0.69 W m^{-2} [Thekaekara, 1976; Ackerman, 1971; Dimitrov and Bar-Nun, 2004]. The unsaturated, polymerizable C_2H_2 , C_2H_4 , HCN, and HC_3N being more abundant at lower altitudes according to the atmospheric $\sim 20 \text{ km}$ scale height, together with the large solar UV flux, makes the atmospheric region between 450 and 150 km a major location for the formation of photochemical polymers, namely aerosols, in addition to the aerosols that rain down from the mesosphere and thermosphere. Thus we devoted our present work to the study of longer wavelength irradiation: Hg lines at 1849 Å $\sim 3.5 \text{ W m}^{-2}$ and 38 W m^{-2} at 2537 Å, from a low pressure mercury lamp.

[6] The photolysis of acetylene was studied in the gas phase by Zelikoff and Aschenbrand [1956], who detected C_2H_4 , C_4H_2 , C_4H_4 , and benzene. Addition of H atoms to acetylene was studied by Callear and Smith [1986], who found C_2H_4 , C_4H_6 , benzene, and linear C_6H_8 (trans-1,3,5-hexatriene) as well as linear C_8H_{10} (1,3,5,7-octatetraene). Tran et al. [2005] photolyzed C_2H_2 in a flow system and observed C_2H_4 , C_2H_6 , C_4H_2 , and C_3H_8 as the principal photoproducts. No polyynes larger than C_4H_2 were observed, presumably because the residence time of the products in the irradiation field in their flow system was short, being adequate for obtaining the chemical mechanism of the initial steps in the photolysis of acetylene and ethylene. However, these photolysis products reside for a long time in Titan's atmosphere and their further photolysis lead to their excitation and further reactions, leading to larger species. Tran et al. [2005] also found that irradiation of ethylene produced mainly the saturated ethane, propane, and butane, as well as low yields of acetylene and diacetylene. Detailed mechanisms for the formation of all the species obtained by photolysis of C_2H_2 and C_2H_4 were presented by Tran et al. [2005], including the effect of CH_4 . Their photolyzing of a Titan composition gas mixture (N_2 : CH_4 : H_2 : C_2H_2 : C_2H_4 : C_3HN = 0.98: 0.018: 0.002: 4×10^{-6} : 3×10^{-6} : 2×10^{-7}), again in a flow system, yielded C_2H_4 , C_2H_6 , C_4H_2 , and C_3H_8 as well as 39 identified compounds [Tran et al., 2005, Table 4], mostly aliphatic hydrocarbons containing double and triple bonds, with much smaller amount of aromatic compounds such as benzene and phenyl acetylene. It should be stressed that these 39 compounds were identified in the gas phase,

while compounds with more than 10 carbon atoms are expected to be in the solid phase. Tran et al. [2003] also analyzed spectroscopically the solid polymers. They found the following functional groups: CH_3 , $\text{C} = \text{C}$, $\text{C} = \text{C} - \text{C} \equiv \text{N}$, and possibly NH. The N:C ratio was found to be 0.057. Vuitton et al. [2006] studied the photolysis of C_2H_2 in the presence of CH_4 and measured the time-dependent decrease in C_2H_2 , the formation and decrease of C_2H_4 and C_3H_6 , and the formation of C_2H_6 .

[7] Coll et al. [1999] employed spark discharges to a N_2/CH_4 mixture and obtained gas phase compounds up to C_5 , which does not include aromatics. Imanaka et al. [2004] used a microwave discharge and identified by spectroscopical methods aliphatic and aromatic hydrocarbons, in addition to amines and nitriles. High-temperature flame studies [e.g., Westmoreland et al., 1989; Wang and Frenklach, 1994, 1997] showed the formation of benzene and other aromatics and provided detailed mechanisms for their formation. Unfortunately, extrapolating these high-temperature studies to the room temperature photolysis regime is rather uncertain.

[8] In the present study, we determined the chemical composition of the gas-phase species as intermediates on the way to the solid phase species by prolonged photolysis of the unsaturated $\text{HC} \equiv \text{CH}$, either alone or in a mixture with $\text{H}_2\text{C} = \text{CH}_2$ and $\text{HC} \equiv \text{N}$, in the presence of CH_4 and N_2 . Obviously, the species detected and their relative abundances are a function of the irradiation time, pressure, and temperature. Pressure is of special importance, since it determines the relative rates of two- body versus three-body reactions. However, in large molecules, the excess energy is dissipated throughout the molecule, unlike in di-, tri-, and tetra-atomic species, where three-body reactions are important. Nevertheless, regardless of the exact formation mechanism, the formation of the gas-phase species suggests the way in which larger species are formed, on their way to the observed solid-state species. In polymer formation energy dissipation among the large number of bonds makes the pressure dependence unimportant. Special care was taken to keep the aerosols free of air from the time of their formation until their analysis, by covering them with hexane.

2. Methods

[9] Several gas mixtures containing C_2H_2 , $\text{C}_2\text{H}_2 + \text{CH}_4$, $\text{C}_2\text{H}_2 + \text{CH}_4 + \text{HCN}$, and $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 + \text{HCN} + \text{CH}_4$, all highly diluted with N_2 up to the pressures shown in the tables were irradiated in spectroil quartz vessels at room temperature. Their compositions are specified wherever the experimental results are shown. For experimental reasons, the mixing ratios of the polymerizable species had to be increased in the reaction mixtures above their values in Titan's atmosphere, in order to obtain measurable quantities of products. Thus the ratio $\text{C}_2\text{H}_2/\text{CH}_4$ was considerably higher, while the ratio $\text{HCN}/\text{C}_2\text{H}_2$ was kept 1:10 as on Titan [Vinatier et al., 2009]. Reactions on the vessel's walls are possible but were not studied. The presence of the majority of the aerosols at the bottom of the irradiation vessel shows that they were formed in the gas phase.

[10] The Spectrosil quartz vessels, 45 cm long and 2 cm in diameter, were cleaned by Alconox, distilled water, and acetone and then inserted for 2 h into a 660°C oven with a

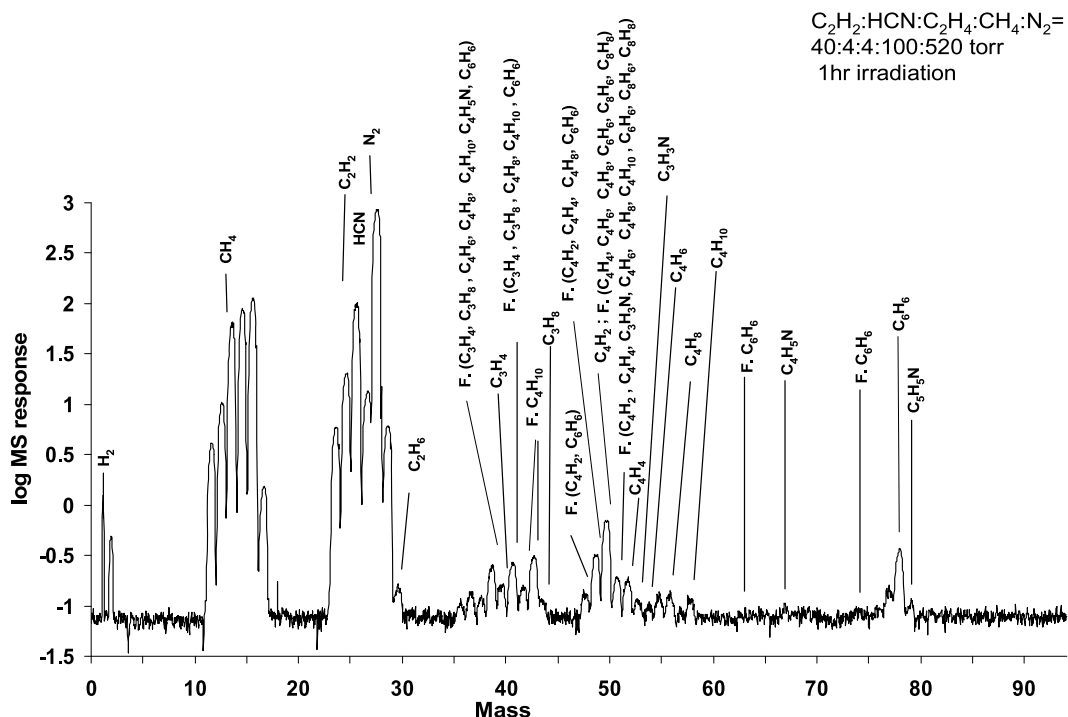


Figure 1. Allocation by the NIST search algorithm of the species to the measured MS peaks. F indicates fragments of the species. Such an agreement was taken as possible proof of the composition of the mixture of products.

constant flow of oxygen, in order to oxidize any remaining organics. The vessel was pumped by a cryopump down to 10^{-6} torr in an all-stainless-steel, mercury-free, vacuum system. The gas mixtures were irradiated by a 23 cm long Pen Ray 3SC-9 low-pressure mercury lamp, emitting a flux of 38 mW cm^{-2} at 2537 \AA and about 10 times less at 1849 \AA , both at a distance of 1 cm from the Spectrosil quartz vessel [Podolak *et al.*, 1979]. C₂H₂, C₂H₄, and HCN absorb

only at 1849 \AA , while the larger products absorb also at 2537 \AA . The irradiation was continued from 15 min up to 72 h. The bottom 5 cm of the vessel was covered by an aluminum foil which blocked further photolysis of the aerosols which settled at the bottom.

[11] About 4 min after the onset of irradiation, a visible fine haze of *pale yellow* aerosols was formed, which settled as a pale yellow deposit at the bottom of the vessel and on

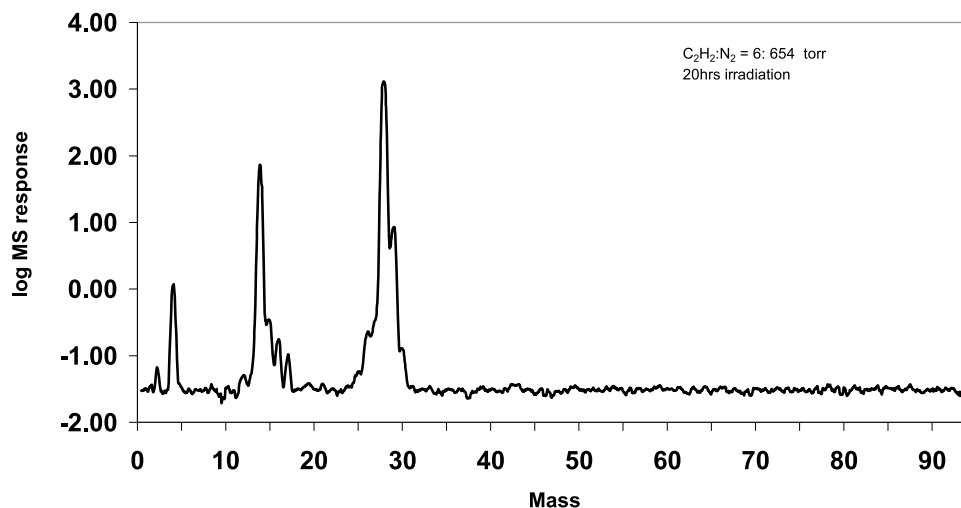


Figure 2. Irradiation for 20 h of an acetylene-poor gas mixture, consisting of C₂H₂:N₂ = 6:665 torr. Note the disappearance of all the intermediates (C₄ species and benzene). The leftover species are mainly C₂H₄, C₂H₆, and its C₂H₅ fragments in the MS with some CH₄ and its fragments CH₂, CH₃ in the MS. Mass 4 is due to He, which is accumulated in the vacuum chamber.

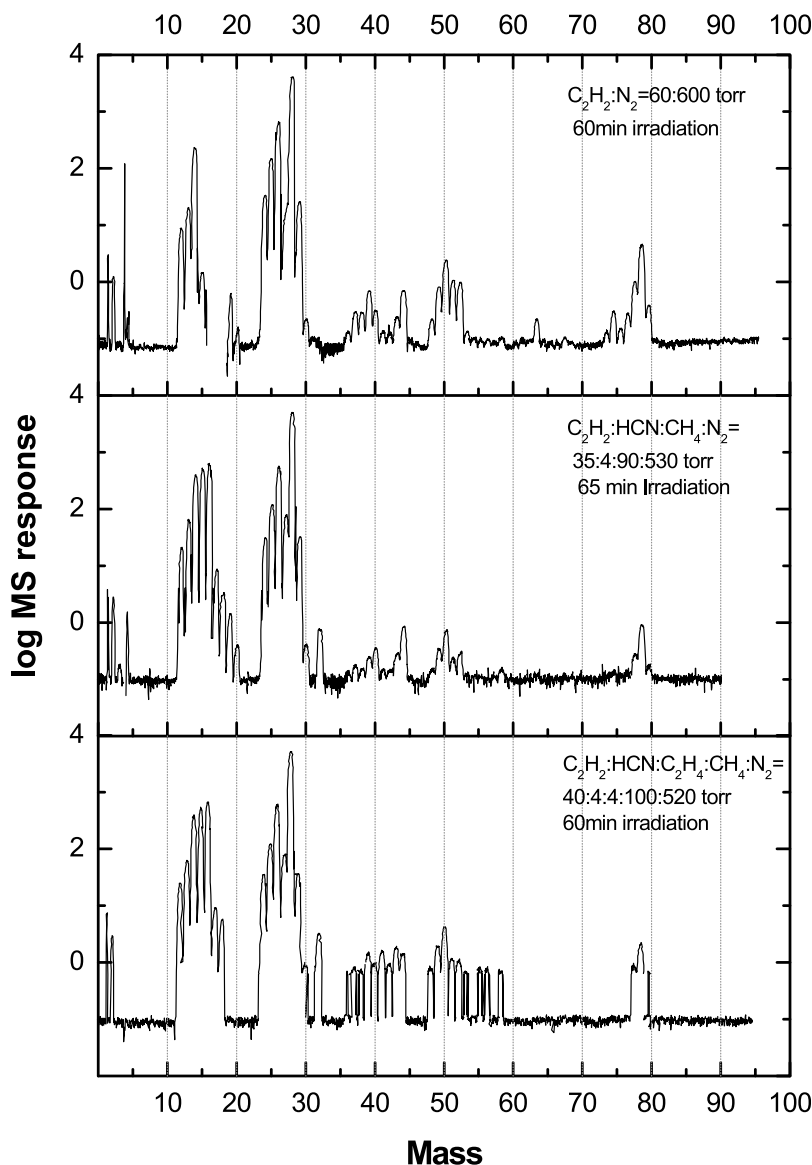


Figure 3. Comparison of the mass spectra of irradiated gas mixtures containing C_2H_2 , $C_2H_2+HCN+CH_4$, and $C_2H_2+C_2H_4+HCN+CH_4$, all highly diluted in N_2 . Note the additional species which were formed when CH_4 , C_2H_4 , and HCN were added.



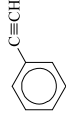
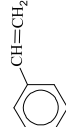
its walls [Bar-Nun *et al.*, 1988]. Upon further irradiation, the pale yellow aerosol became slightly darker but never reddish like the Tholins formed by spark or silent discharges, which contain many $C\equiv N$ groups, according their high N:C ratio.

[12] The vessel was then connected to a vacuum system and the irradiated gas mixture was analyzed without gas chromatography (GC) separation by a Riber Model QX-100 quadrupole mass filter. The MS spectra were compared with the known compounds included in the National Institutes of Standards and Technology (NIST) 98 mass spectral library using the NIST search algorithm. In this procedure, the entire mass spectrum, including all components, is to be fitted. An exact fitting meant an identification of all the parent molecule and their fragments. Another analysis separated the products starting from C_4 species, on a GC using a Porapak N column, followed by a Hewlett-Packard MSD 5970 mass spectrometer. Again, each gas chromatograph

peak gave a suit of fragment peaks in the mass spectrometer, which were compared with the NIST 98 mass spectral library, using the NIST search algorithm. To ascertain their fragmentation pattern and sensitivities, benzene, phenyl acetylene, and styrene were injected separately. These GC-MS analyses established the formation of C_4H_4 , C_4H_6 , C_6H_6 , C_8H_6 , and C_8H_8 and their relative abundances under the experimental condition.

[13] The aerosols were collected at the bottom of the irradiation vessel in a micro glass vial (10×2 mm), which was covered at the end of the irradiation, under vacuum, by *n*-hexane and delivered without exposure to air to a Supersonic GC-MS analysis [Fialkov and Amirav, 2004]. In this method of GC-MS analysis, the entire sample is evaporated and carried by a fast flow of He, carrying with it large-molecular-weight compounds and separating them on a GC column. The beam is passed through a supersonic

Table 1. Gas Phase Species Produced by UV Photolysis

Species	Structure	Common Name	Abundance (%)		
			C ₂ H ₂ ; N ₂ = 85: 600 torr Irradiated for 60 min	HCN:C ₂ H ₂ :CH ₄ : N ₂ = 4:35: 90: 530 torr Irradiated for 60 min	HCN:C ₂ H ₄ :C ₂ H ₂ :CH ₄ : N ₂ = 4:4:40: 130:500 torr Irradiated for 65 min
H ₂	H-H	Hydrogen	4.1	47.1	19.4
CH ₄		Methane	14.9		
C ₂ H ₂	HC≡CH	Acetylene		Reactant	Reactant
HCN	HC≡N	Hydrogen cyanide		Reactant	reactant
C ₂ H ₄ ^a	H ₂ C = CH ₂	Ethylene	+		reactant
N ₂	N≡N	Nitrogen		Background	
C ₂ H ₆	H ₃ C-CH ₃	Ethane	7.4	18.1	15.7
C ₃ H ₄	H ₃ C-C≡CH	Methyl acetylene	2.6	4.5	4.4
C ₃ H ₆	H ₂ C = CH-CH ₃	Propene	0.1	-	-
C ₃ H ₈	H ₃ C-CH ₂ -CH ₃	Propane	-	9	2.4
C ₄ H ₂ ^b	H ₃ C-CH ₂ -C≡CH	Diacetylene	15.9	0.4	24.2
C ₄ H ₄ ^b	HC≡C-C≡CH	Vinyl acetylene	1.6	0.7	0.5
C ₄ H ₆ ^b	HC≡C-CH = CH ₂	Divinyl	0.5	-	0.5
C ₄ H ₈	H ₂ C = CH-CH = CH ₂	Butene	-	-	4.8
C ₄ H ₁₀	H ₂ C = CH-CH ₂ -CH ₃	Butane	2.1	4.5	4.8
C ₄ H ₁₀	H ₃ C-CH ₂ -CH ₂ -CH ₃	Isobutane	0.8	-	7.5
					
C ₆ H ₆ ^b		Benzene	46.1	13.6	14.6
C ₈ H ₆ ^b		Phenyl acetylene	3.2	0.9	1.0
C ₈ H ₈ ^b		Styrene	0.7	0.2	0.2
C ₂ N ₂	N≡C-C≡N	Cyanogen	-	Trace	Trace
HC ₃ N	HC≡C-C≡N	Cyanoacetylene	-	Trace	Trace
C ₃ H ₃ N	H ₂ C = CH-C≡N	Vinylcyanide	-	0.5	0.5
Total			100	100	100

^aC₂H₄ could not be detected in the presence of large excess of N₂. Therefore, without quantitative determination of C₂H₄, the percentages of the products are indicative only of their importance.

^bThese species were detected by their separation on a GC column and analysis by MS. Their relative abundances were determined by their NIST reported MS sensitivities, which were checked against the *pure* substances (benzene, phenyl acetylene, and styrene). The other species that were not injected separately into the GC were given their NIST sensitivities and, hence, abundances.

Table 2. Solid Phase Species Produced by UV Photolysis of C₂H₂

Mass	Formula	Structure ^a	Name	Amount (%)
50	C ₄ H ₂		Diacetylene	0.1
92	C ₇ H ₈		Toluene	3.2
100	C ₇ H ₁₆		Heptane	0.2
102	C ₈ H ₆		Phenylacetylene	6.1
104	C ₈ H ₈		Styrene	0.1
106	C ₈ H ₁₀		Ethylbenzene	0.2
116	C ₉ H ₈		Benzene 1-propynyl	0.4
118	C ₉ H ₁₀		Benzene 2-propenyl	0.5
128	C ₁₀ H ₈		Naphthalene	11.0
132	C ₁₀ H ₁₂		Benzene, 3-butenyl	0.6
142	C ₁₁ H ₁₀		Naphthalene 1 or 2-methyl	0.9
154	C ₁₂ H ₁₀		Biphenyl	73.0
168	C ₁₃ H ₁₂		Biphenyl 3-methyl	0.7
178	C ₁₄ H ₁₀		Phenanthrene	1.1
180	C ₁₄ H ₁₂		1,2-Diphenylethylene	0.7
182	C ₁₄ H ₁₄		Biphenyl 1,3-dimethyl	0.1
192	C ₁₅ H ₁₂		Phenanthrene, 3-methyl	0.1
204	C ₁₆ H ₁₂		2-Phenylnaphthalene	0.1
230	C ₁₈ H ₁₄		Pyrene, 1,9-dimethyl	0.7
252	C ₂₀ H ₁₂		Perylene	0.1
252	C ₂₀ H ₁₂		Benzo(a)pyrene	0.1
252	C ₂₀ H ₁₂		Benzo(e)pyrene	0.1
Up to 882 ^b				
Total				100%

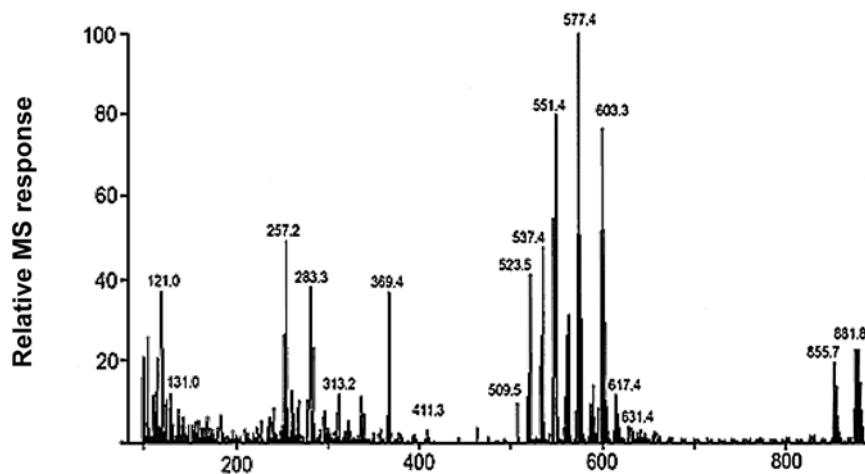


Figure 4. A DCI mass spectrum of the solid aerosols. Being in contact with air, these might have been oxidized to some extent.

nozzle into vacuum, followed by a skimmer. Most of the heavier molecules pass through; while the lighter He is deflected. Thus the heavier organics are enriched before reaching the MS. In this analysis the entire sample was analyzed including the solid phase and not only the materials dissolved in *n*-hexane. In other analyses by Fialkov and Amirav this method was able to detect coronen ($C_{24}H_{12}$), a 7-ring polycyclic aromatic hydrocarbon (PAH) with a molecular weight of 300 daltons. Apparently, benzo[a]pyrene (5 condensed rings with $C_{20}H_{12}$, $m/e = 252$) is the largest detectable polyaromatic hydrocarbon formed in our experiments. Data analysis was performed with Chemstation software in combination with the NIST mass spectral library, using the NIST search algorithm.

[14] Another analysis, DCI (direct desorption chemical ionization), employs evaporation of the sample by a hot wire heated fast to 200°C up to 400°C at 10^{-6} torr. This method could break large polymers and the vaporized polymer fractions were ionized by isobutene plasma and analyzed by MS.

[15] A microelemental analysis by burning the sample was carried out on many aerosol samples as well.

3. Experimental Results and Discussion

3.1. Gas-Phase Species

[16] The mass spectrum of the *gas phase* photolysis products of a gas mixture consisting of $C_2H_2:C_2H_4:HCN:CH_4:N_2 = 40:4:4:100:520$ irradiated for 60 min without GC separation is shown in Figure 1.

[17] Prolonged irradiation of an acetylene-poor gas mixture shows in Figure 2 that all the intermediate species up to $m/e = 90$, which is the limit of our quadrupole mass filter, disappear. In particular, heavier hydrocarbons polymers are

formed at the expense of the smaller ones. The addition of HCN to the gas mixture (Figure 3) resulted mainly in the production of vinylcyanide, an adduct of HCN to C_2H_2 , cyanoacetylene, and cyanogen. The addition of C_2H_4 to the gas mixture resulted mainly in the production of propane, butane, and isobutane.

[18] Table 1 presents a summary of the species found by the mass spectrum of three representative irradiated gas mixtures. The contribution of CH_4 , C_2H_4 , and HCN to the case of pure C_2H_2 is shown as well. Obviously, the relative abundances of the various species is a function of the irradiation time and is merely indicative of their importance as intermediate gas-phase species. As mentioned above, all but C_2H_6 , C_2H_4 , and CH_4 disappear when an acetylene-poor gas mixture is irradiated for a long time (Figure 2).

[19] The absence of linear C_6 suggests that benzene, the most abundant species, is formed readily whenever a conjugated C_6 species is formed. However, for lack of kinetic data, this remains as a mere suggestion.

3.2. Solid-Phase Species

[20] The determination of the chemical composition of the aerosols was the main purpose of this study, while the study of the gas-phase species was a mere prelude, which could show the pathways by which the solids are formed. *Zelikoff and Aschenbrand* [1956] found that the quantum yield for C_2H_2 disappearance is two orders of magnitude larger than the quantum yields for production of C_4 species, showing that most of the acetylene forms large polymers, which did not show up in their analyses of the gas phase. At low acetylene pressure (1.67 torr), their quantum yield of benzene formation dropped sharply, while the yields of diacetylene and vinylacetylene remained approximately the same.

Notes to Table 2:

Note. A gas mixture consisting of $C_2H_2:Ar = 70:650$ torr was irradiated for 24 h, covered by hexane under vacuum and delivered to a Supersonic GC-MS analysis without exposure to air. The entire mixture of solids and hexane soluble materials was injected into the Supersonic GC-MS.

^aIt is possible that some of the isomers identified could be a mixture of isomers.

^bA fraction of cross-linked linear chains was not analyzable by the supersonic GC-MS method. A DCI analysis as described below showed masses up to 882.

[21] Table 2 summarizes the hydrocarbons detected by the Supersonic GC-MS analysis. Comparing the species detected in the gas phase as shown in Table 1, we find in both tables diacetylene, phenyl acetylene, and styrene, which were dissolved to some extent in the polymers. Again, as suggested above, C_6 species are bound to form the observed benzene, phenyl acetylene, styrene, naphthalene, phenanthrene, perylene, and benzopyrene. It should be mentioned that although the supersonic GC-MS could detect species up to $m/e = 300$, the largest species detected was benzopyrene at $m/e = 252$.

[22] The list of analyzed solid-state products shown in Table 2 favors aromatics as the main components of the solid phase aerosols which are formed in our experiments. However, many repeated microelemental analyses of the aerosols produced from C_2H_2 diluted in an inert gas such as Ar or Xe ($C_2H_2:Ar = C_2H_2:Xe = 600:60$) showed consistently $C:H = 1.013 \pm 0.001$, while the list of compounds in Table 2 gives a ratio of $C:H = 1.2$. This discrepancy suggests that some H-rich compounds are also present. A complete kinetic analysis of the polymerization of acetylene via the adequate kinetic model, was performed by *Dimitrov and Bar-Nun* [1997, 2004]. In this kinetic scheme, acetylene photolysis results mainly in formation of linear polymers, such as vinyl acetylene $HC\equiv C-(CH=CH)_n-CH=CH_2$ and polyvinyl $H_2C=CH-(CH=CH)_n-CH=CH_2$. These two have a ratio $C:H \approx 1$ and can lower the $C:H$ from the 1.2 of Table 2 to the measured 1.013 ± 0.001 . Apparently, polyynes $HC\equiv C-(C\equiv C)_n-C\equiv CH$, with its high $C:H$ ratio, is not an important component of these long chain linear polymers. The polymerization proceeds via Diels-Alder low-temperature diene synthesis, with an activation energy of $0-1 \text{ kcal mole}^{-1}$. Since in the conjugated double and triple bonds the π electrons hybridize along the chain, the polymers can cross-link to form a hard three-dimensional matrix [*Dimitrov and Bar-Nun*, 2002, 2003]. This matrix cannot be analyzed by the supersonic GC-MS analysis and avoids detection, leaving a fraction of the species undetected. However, DCI found materials with $m/e = 121, 257, 283$, and 370 together with clusters of heavier materials with $m/e = 524, 538, 552, 578$, and 604 and at $m/e 856$ and 882 (Figure 4). The separation by 26 and 14 amu is possibly due to detachment of H-rich C_2H_6 and CH_2 . The largest mass, 882 with $C:H = 1$, would correspond to $C_{68}H_{68}$. These are likely the cross-linked linear polymers, proposed by *Dimitrov and Bar-Nun* [2002, 2003], which break on the hot wire during the DCI analysis. We have no positive analysis of their composition, except the measured elemental analysis of $C:H \approx 1$ rather than the higher aromatic ratio and their insolubility. The small amounts of the most abundant species in the supersonic GC-MS analysis, biphenyl ($m/e = 154$) and naphthalene ($m/e = 128$), suggest that the species listed in Table 2 are overwhelmed by the cross-linked linear polymers, as the adequate kinetic model of *Dimitrov and Bar-Nun* [1997, 2004] suggests.

4. Conclusions

[23] A large fraction of the major unsaturated species, C_2H_2 , C_2H_4 , HCN, and HC_3N with mixing ratios of about

3×10^{-6} , $10^{-7}-10^{-8}$, 3×10^{-7} and $10^{-9}-10^{-10}$, reside in Titan's stratosphere between 150 and 500 km [*Vinatier et al.*, 2009; *Coustenis et al.*, 2007] before they condense in the tropopause. They also pass this barrier and fill the warmer troposphere, as shown by the abundant C_2H_6 on the surface. Also, a large flux of medium-wavelength UV penetrates down to these levels, resulting in the polymerization of these unsaturated compounds and the formation of aerosols. Therefore, in addition to the formation of aerosols in the thermosphere at about 1000 km and their raining down, we devoted our experiments to aerosol formation at altitudes of about $150-500 \text{ km}$, where both abundances and solar UV flux are high, bearing in mind that additional photolysis may occur in the even denser lower stratosphere and troposphere.

[24] In the gas phase, C_2H_2 photolysis results in unsaturated C_4 species which, on further addition of C_2 , form cyclic benzene (C_6H_6). All these gas-phase species disappear when an acetylene-poor gas mixture is irradiated for a long time, giving rise to larger solid-state species that consist mainly of biphenyl, naphthalene, and phenanthrene. The species distribution in the solid phase suggests that the mechanism of formation of condensed rings involves addition of C_2 and ring closure. The largest solid phase species formed was the condensed 5-ring benzopyrene but not the 7-ring coronen, which could have been detected there.

[25] Another, even larger, fraction of the polymers apparently consists of polyvinyl and vinyl acetylene chains, as suggested by *Dimitrov and Bar-Nun* [1997, 2004] which are cross-linked due to their labile π electrons and form an insoluble solid matrix. This explains the reduction of the $C:H$ ratio from the condensed aromatics of 1.2 to the measured $C:H = 1.013 \pm 0.001$ of the polymers. The cross-linked polyvinyl chains will be insoluble in the recently confirmed CH_4/C_2H_6 lakes [*Stofan et al.*, 2007; *Brown et al.*, 2008] of Titan. This cross-linking may account also for the hardening of the semiliquid aerosols in Titan's atmosphere [*Bar-Nun et al.*, 1988; *Dimitrov and Bar-Nun*, 2002, 2003] and their not sticking to the windows and ports of the Huygens probe.

[26] The nitrogen content of the pale yellow aerosols obtained with the Titan proportion of C_2H_2 : HCN = $10:1$, was $C:H:N = 1:1:0.007(8)$. This suggests that HCN is not incorporated easily into the mostly hydrocarbon polymers. This in contrast to the nitrogen-rich reddish aerosols formed by spark or silent (microwave) discharges [*Coll et al.*, 1999; *Israël et al.*, 2005; *Khare et al.*, 1984]. This difference stems from the large number of atoms, radicals, and ions produced in the discharge, which introduce into the polymers a large proportion of CN, versus the mild UV photolysis. *Bellucci et al.* [2009] also found by comparing the transmission spectra of fractal aerosol particles in Titan's atmosphere with fractal aggregates of Tholins, having the optical properties *Khare et al.*'s [1984], that there are important chemical differences between the actual haze particles and Tholins; namely the N-H and $C\equiv N$ absorption bands of Tholins do not appear in their data.

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