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Photochemical processes on Titan. Irradiation of mixtures of gases that simulate Titan's atmosphere

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Abstract

Photochemical reaction pathways in Titan's atmosphere were investigated by irradiation of the individual components and the mixture containing nitrogen, methane, hydrogen, acetylene, ethylene, and cyanoacetylene. The quantum yields for the loss of the reactants and the formation of products were determined. Photolysis of ethylene yields mainly saturated compounds (ethane, propane, and butane) while photolysis of acetylene yields the same saturated compounds as well as ethylene and diacetylene. Irradiation of cyanoacetylene yields mainly hydrogen cyanide and small amounts of acetonitrile. When an amount of methane corresponding to its mixing ratio on Titan was added to these mixtures the quantum yields for the loss of reactants decreased and the quantum yields for hydrocarbon formation increased indicative of a hydrogen atom abstraction from methane by the photochemically generated radicals. GC/MS analysis of the products formed by irradiation of mixtures of all these gases generated over 120 compounds which were mainly aliphatic hydrocarbons containing double and triple bonds along with much smaller amounts of aromatic compounds like benzene, toluene and phenylacetylene. The reaction pathways were investigated by the use of ^{13}C acetylene in these gas mixtures. No polycyclic aromatic compounds were detected. Vapor pressures of these compounds under conditions present in Titan's atmosphere were calculated. The low molecular weight compounds likely to be present in the atmosphere and aerosols of Titan as a result of photochemical processes are proposed.

Keywords: Photochemistry; Titan; Atmosphere composition; Organic chemistry; Abundances atmosphere

1. Introduction

The Cassini probe has reached the Saturn system and is investigating Saturn and its moons. Of particular interest is Titan, the largest moon of Saturn, which is unique in having a dense atmosphere consisting mainly of nitrogen (98%), methane (2%). It has been determined that solar UV radiation is the predominant energy source impinging on Titan (Sagan and Thompson, 1984; Tran et al., 2003b). Minor components of Titan atmosphere including hydrogen, ethane, acetylene, ethylene, cyanoacetylene, and hydrogen cyanide are probably formed by the action of solar radiation and Saturn's magnetosphere electrons on methane. The atmospheric chemistry proceeding in Titan's atmosphere is an ongoing formation of complex structures from methane, a process relevant to but probably not identical with, reactions that led to the origins of life on Earth (Clarke and Ferris, 1997a).

Laboratory simulations of the effect of solar UV on the gas mixtures representative of Titan's atmosphere were performed in a flow system (Tran et al., 2003b). In these studies, a reactant mixture that corresponds to the composition of Titan's atmosphere at the north pole was photolyzed by UV radiation (Table 1). In winter, the atmosphere at the pole is partially protected from solar radiation as a consequence of the 20° tilt of Titan's axis (Yung, 1987) while photolysis of

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the same compounds at Titan's equator, where there is no protection from the solar UV, results in much lower mixing ratios for most of the atmospheric constituents (Coustenis et al., 1993; Coustenis and Bezard, 1995).

The objective of this research is to determine the role of UV light on the formation of volatile reaction products in Titan's atmosphere. Knowledge of the structures, mechanisms of formation and relative abundances of these compounds will provide insight into the relative importance of UV radiation and magnetospheric electrons in the formation of organics in Titan's atmosphere. These data will suggest the compounds likely to be present in the aerosols there. The structures of the volatile products provide indirect evidence of the structural units in Titan's haze. Finally, this information will be useful in the interpretation of the mass spectral and spectroscopic data obtained by the Huygens probe.

The photochemical reactions were performed in a flow reactor using a low-pressure mercury lamp with principal emissions at 185 and 254 nm as the light source. This radiation is not absorbed by methane or nitrogen but is absorbed by acetylene, ethylene and cyanoacetylene. Some of the photoproducts of these gases absorb the 254 nm radiation (Clarke and Ferris, 1996). The structures of the photoproducts were determined by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS). The quantum yields (QY) of formation of the photoproducts were determined. The reaction products formed are compared with those formed in discharge reactions in order to determine the relative roles of UV light and magnetospheric electrons in the formation of more complex products in Titan's atmosphere.

2. Experimental

A photochemical flow reactor has been used to study the photochemistry of gaseous mixture. The design of the flow line and preparation of gas mixtures were described previously (Clarke et al., 2000; Tran et al., 2003a). A constant flow rate of 15 cm^3/min at a temperature of 297 K and a pressure of 700 ± 20 Torr was maintained in the flow reactor and the gases were irradiated by a low pressure mercury lamp, with principal emissions at 185 and 254 nm (Clarke and Ferris, 1997a). The volatile products were condensed in cold traps, cooled by liquid nitrogen, consisting of Pyrex coils 5 mm in diameter and 10 m in total length. The volatile products were then transferred to a sample cylinder and pressurized with pure nitrogen gas for GC and GC/MS analysis. Figures showing GC and GC/MS traces are in the Supplementary material.

2.1. Analysis of volatiles and polycyclic aromatic hydrocarbons (PAHs)

The volatile products were analyzed by a Hewlett Packard 5890 GC equipped with a 10-port valve Inlet System, model 4C10WT (Valco Instrument Co. Inc.). Two different operating conditions were performed to analyze the hydrocarbons and nitrile compounds. A flame ionization detector (FID) was employed to analyze hydrocarbons using a Supelco Alumina PLOT gas chromatography column (30 m × 0.53 mm ID, 25µ film thickness) and a nitrogen–phosphorous detector (NPD) was employed to analyze the nitrile compounds using a Restek RTX-502.2 capillary column (105 m × 0.53 mm ID, 3µ film thickness). The GC was operated under the following conditions: 3 min isothermal at 35 °C, a gradient of 8 °C/min up to 140 °C, 8 min isothermal at 140 °C, 50 °C/min up to 200 °C. GC/MS was performed on a Hewlett Packard 6890/5973 GC/MS system using a Restek RTX 502.2 capillary column (60 m length, 0.32 mm ID). The mass spectrometer was operated at an ionization voltage of 70 eV to scan a mass range from 35 to 350 AMU at a sampling rate of 2.4 scans per second. The organic compounds were identified using a NIST 98.1 Mass Spectrum library.

The formation of polycyclic aromatic hydrocarbons (PAHs) in the flow reactor after irradiation was investigated by extraction with high purity dichroromethane. The extract was initially concentrated to 1.0 ml and after GC/MS, the residual 0.8 ml was concentrated to 0.1 ml for HPLC analysis. The PAHs were analyzed following the compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air (Hodgeson et al., 1990; Winberry and Jungclaus, 1999).

2.2. Quantum yield determination

The gas reactants of the flow control (non-irradiated) and photoproducts formed during the course of the flow irradiated were trapped in pyrex glass coil traps using liquid nitrogen, and analyzed by GC to determine the amount of each trapped at different times. The quantum yield (QY) of loss of gas reactant was determined from the difference in the amounts trapped in the control reaction and that for the irradiation reaction. The QY of formation of a photoproduct is the ratio of the recovered rate of product formed during the irradiation process to the number of photons of light absorbed by the reactant, which is primarily responsible for that material's production (Clarke et al., 2000). The QYs were determined with a 14% uncertainty.

2.3. Recovery of reactants in control studies

The efficiency of gas recovery has been performed in the flow line in order to evaluate the capacity of the cold traps and the recovery yield of the gaseous reactants and products at liquid nitrogen temperature (−196 °C). CH_4 has a vapor pressure of approximately 10 Torr at liquid nitrogen temperature and hence is pumped out of the cold traps during the course of the flow reaction. Hydrogen is not condensable at liquid nitrogen temperature.

A mixture of alkanes or alkenes at the concentration of 15 ppm each in nitrogen was passed through the flow reactor at the flow rate of 15 ml/min and was trapped in a coil trap cooled to liquid nitrogen temperature. After a predetermined time had elapsed, the flow was shut off and GC was used to quantify the trapped products. The recovery of ethane was linear up to 1 µmol (30 µg) while that of propane and butane was linear up to 2 µmol and more than 95% of the latter gases were recovered (Fig. 1a). The upper limit of ethylene that could be trapped was 0.6 µmol (16.8 µg) while more than 95% of the propene, butene and acetylene were trapped (Fig. 1b).

The low recovery yields of C_2H_6 and C_2H_4 are attributed to their inability to condense out of the gas phase as they were flowing through the two cold traps due to their low sticking probability (Atkins, 1990). The sticking probability, P_s, is defined as

$$P_s = R_{ad}/R_c,$$

where R_{ad} is adsorption rate of gas by the surface of the coil traps, R_c is collision rate of gas with the trapping surface. A gas has high recovery yield when its sticking probability is close to unity. The sticking probability is different for every gas and therefore, in a mixture of gases, there will be competition for the vacant sites on the surface. Despite low recovery, the concentrations of C_2H_4 used are below the sticking probability limit.

3. Results and discussion

The compounds produced in Titan's atmosphere by solar UV radiation depend not only on the products formed by the irradiation of the individual components, but also on the subsequent reactions of these initial products with other atmospheric constituents. Insight into the extent of the reactions with the other atmospheric constituents was obtained by comparison of the products formed from the photolysis of individual constituents with those formed from the photolysis of the same compounds in the presence of other constituents of Titan's atmosphere (Table 1).

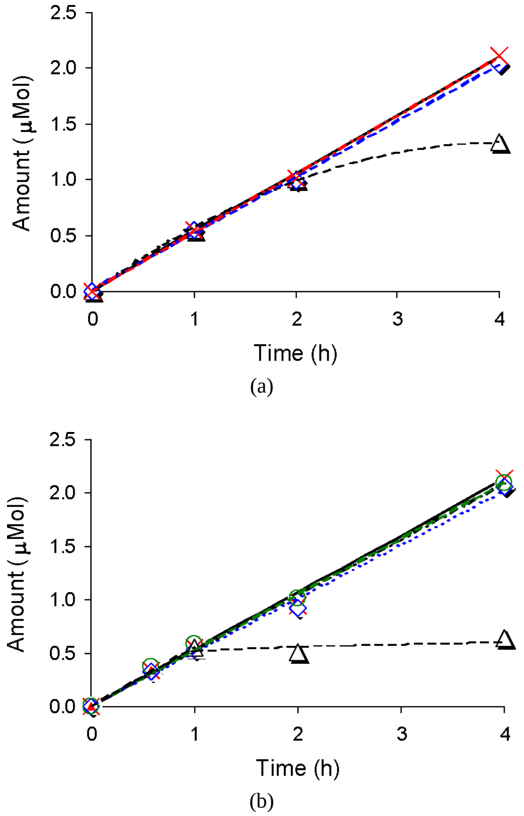


Fig. 1. Standard calibration plots for the gas chromatographic analysis of the gases condensed in liquid nitrogen trap in the flow reactor. Reactants and products were used in amounts only where there was a linear correlation between the amount and flow time as shown by the solid line. (a) C_2H_6 (△), C_3H_8 (◇), C_4H_{10} (×); and (b) C_2H_4 (△), C_3H_6 (×), C_4H_8 (◇), C_2H_2 (○).

3.1. *Photolysis of acetylene, ethylene, and their mixture*

The quantum yield for acetylene loss obtained by the irradiation of nitrogen:acetylene (1:3.4 × 10^{-6}) gas mixture (experiment 1, Table 2) was 1.1. Analysis of the products by gas chromatography revealed the presence of ethane, ethylene, propane, butane and diacetylene as the principal photoproducts. Diacetylene was formed from the addition of the ethynyl radical ($\cdot C_2H$) with acetylene (1), (2) while the

Table 1
Comparison of experimental mixing ratios[a] to those on Titan[b]

Experiment	Mixing ratio[a]					
	Nitrogen	Methane	Hydrogen	C_2H_2	C_2H_4	HC_3N
1	1	–	–	3.4 × 10^{-6}	–	–
2	0.97	0.03	–	3.4 × 10^{-6}	–	–
3	1	–	–	–	3.3 × 10^{-6}	–
4	1	–	–	3.9 × 10^{-6}	3.6 × 10^{-6}	–
5	1	–	–	–	–	1.7 × 10^{-6}
6	0.98	0.02	–	–	–	1.2 × 10^{-6}
7	0.98	0.018	0.002	4 × 10^{-6}	3 × 10^{-6}	2 × 10^{-7}
Titan[b]	0.98	0.018	0.002	3.5 × 10^{-6}	3.0 × 10^{-6}	1.7 × 10^{-7}

[a] The experimental mixing ratios are determined with 10% uncertainty.
[b] Average of values reported at 70° north latitude for altitudes corresponding to pressure of 0.1 and 1.5 mbar (Coustenis et al., 1993).

Table 2
Quantum yields for the photolysis of (1) nitrogen:acetylene mixture, (2) nitrogen:methane:acetylene mixture, (3) nitrogen:ethylene mixture, and (4) nitrogen:acetylene:ethylene mixture. The negative values indicate QYs loss while the positive ones indicate the QYs formation. The QYs were determined with 14% uncertainty

Experiment	QY					
	C_2H_2	C_2H_4	C_2H_6	C_3H_8	C_4H_{10}	C_4H_2
1	−1.1	0.02	0.02	0.01	<0.01	<0.01
2	−0.45	0.08	0.40	0.04	<0.01	<0.01
3	0.12	−3.2	0.40	0.11	0.05	0.01
4	−0.73	−2.7	0.37	0.12	0.06	0.01

saturated hydrocarbons were formed from the irradiation of ethylene, which was generated in the addition of hydrogen atoms to acetylene (3) and the disproportination of the resulting vinyl radical (4).

$$HC{\equiv}CH \xrightarrow{h\nu} HC{\equiv}C\bullet + H\bullet, \tag{1}$$

$$HC{\equiv}C\bullet + HC{\equiv}CH \rightarrow HC{\equiv}C\text{–}C{\equiv}CH + H\bullet, \tag{2}$$

$$HC{\equiv}CH + \bullet H \rightarrow \bullet CH{=}CH_2, \tag{3}$$

$$\bullet CH{=}CH_2 + \bullet CH{=}CH_2 \rightarrow H_2C{=}CH_2 + CH{\equiv}CH. \tag{4}$$

No polyacetylenes longer than diacetylene were observed as reaction products. This may be because they were not formed or because they are unstable at 298 K (de Vanssay et al., 1995; Coll et al., 1999a). It has been proposed that the formation of triacetylene is initiated either by the reaction of the metastable triplet excited state of diacetylene with acetylene or by the reaction of the ethynyl radical ($\cdot C_2H$), formed by acetylene photolysis, with diacetylene (Zwier and Allen, 1996). In both instances there is ethylene and other unsaturated compounds present in Titan's atmosphere that will also react with these activated intermediates. These reactions will limit the amounts of polyacetylenes formed by either of the proposed reaction pathways.

When the same photolysis was performed in the presence of methane (experiment 2, nitrogen:methane:acetylene, $0.97{:}0.03{:}3.4 \times 10^{-6}$) the quantum yield for acetylene loss dropped to 0.45 and the quantum yields for ethane and ethylene formation increased 20- and 4-fold, respectively (Table 2). These findings are consistent with the photochemical loss of a hydrogen atom from acetylene followed by abstraction of a hydrogen atom from methane by the ethynyl radical to regenerate acetylene (Yung et al., 1984) (5). Combination of two methyl radicals generates ethane (6). The ethylene is formed by the addition of hydrogen atoms to acetylene to generate radicals that disproportionate to ethylene and acetylene (3), (4).

$$HC{\equiv}C\bullet + CH_4 \rightarrow HC{\equiv}CH + \bullet CH_3, \tag{5}$$

$$2\bullet CH_3 \xrightarrow{M} CH_3CH_3. \tag{6}$$

Photolysis of a nitrogen:ethylene ($1{:}3.3 \times 10^{-6}$) mixture (experiment 3, Table 2) yielded the saturated hydrocarbons ethane, propane and butane as well as low yields of acetylene and diacetylene. The high quantum yield for ethylene loss (3.2) is consistent with a chain reaction, which resulted from the efficient reaction of the radicals formed by the photolysis of ethylene with other ethylene molecules. Initially, the photolysis of ethylene generates excited state species, which are deactivated by the 700 Torr pressure in the flow reactor to generate vinyl radicals and acetylene (7), (8) (Balko et al., 1992). The hydrogen atoms formed by photolysis of ethylene and the other reactants add to ethylene to give ethyl radicals (9). The ethyl radicals can combine to give *n*-butane (10), react with hydrogen atoms to give ethane (11) or dissociate to give methyl radicals (12). The subsequent reactions of these radicals with ethylene give the wide array of products observed in the photolysis of ethylene and suggest that it is the precursor of the bulk of the hydrocarbons observed in the atmosphere of Titan (9)–(14) (Grioux et al., 1989),

$$H_2C{=}CH_2 \xrightarrow{h\nu} \bullet CH{=}CH_2 + H\bullet, \tag{7}$$

$$CH_2{=}CH_2 \xrightarrow{h\nu} HC{\equiv}CH + 2H\bullet \text{ or } H_2, \tag{8}$$

$$CH_2{=}CH_2 + H\bullet \xrightarrow{M} \bullet CH_2CH_3, \tag{9}$$

$$2\bullet CH_2CH_3 \xrightarrow{M} CH_3CH_2CH_2CH_3, \tag{10}$$

$$H\bullet + \bullet CH_2CH_3 \xrightarrow{M} CH_3CH_3, \tag{11}$$

$$H\bullet + \bullet CH_2CH_3 \xrightarrow{M} 2CH_3\bullet, \tag{12}$$

$$\bullet CH_3 + \bullet CH_2CH_3 \rightarrow CH_4 + H_2C{=}CH_2, \tag{13}$$

$$\bullet CH_2CH_3 + \bullet CH_2CH_3 \rightarrow H_2C{=}CH_2 + CH_3CH_3. \tag{14}$$

The emphasis in many studies of the atmospheric chemistry of Titan focuses on the reactions of acetylene (Shindo et al., 2003). However, the quantum yields for ethylene loss (3.2) compared to that of acetylene loss (1.1) obtained in this study also supports our claim that ethylene photolysis is an important source of higher molecular weight hydrocarbons.

A mixture of nitrogen, acetylene and ethylene ($1{:}3.9 \times 10^{-6}{:}3.6 \times 10^{-6}$) in experiment 4 was irradiated to gain further insight into the sources of the reaction products (Table 2). The quantum yields for the loss of acetylene (0.73) and ethylene (2.7) decreased from that observed when they were irradiated individually (acetylene 1.1 and ethylene 3.2) indicative of the regeneration of some of the original starting compounds after they were dissociated into radicals by UV light (15). The close correlation of the quantum yields for the formation of ethane, propane and butane in the mixture of acetylene and ethylene with the quantum yields for

Table 3
Quantum yields for the photolysis of (5) nitrogen:cyanoacetylene mixture, (6) nitrogen:methane:cyanoacetylene mixture, and (7) a representative mixture of Titan gases including nitrogen, methane, hydrogen, acetylene, ethylene, and cyanoacetylene. The negative values indicate QYs loss while the positive ones indicate the QYs formation. The QYs were determined with 14% uncertainty

Experiment	QY								
	HC_3N	HCN	CH_3CN	C_2H_2	C_2H_4	C_2H_6	C_3H_8	C_4H_{10}	C_4H_2
5	−2.3	0.23	<0.01	<0.01	0.05	0.04	<0.01	N.D.	N.D.
6	−1.8	0.28	0.01	0.04	0.05	0.34	0.02	N.D.	N.D.
7	−2.2	0.99	0.03	−0.08	−1.5	0.44	0.25	0.04	N.D.

N.D.: Not detected.

their formation from ethylene suggests that ethylene is the principal source of these hydrocarbons.

$$HC{\equiv}C\bullet + H_2C{=}CH_2 \rightarrow HC{\equiv}CH + H_2C{=}CH\bullet. \quad (15)$$

3.2. Cyanoacetylene photolysis

A mixing ratio of cyanoacetylene comparable to that of acetylene and ethylene was chosen so that it was possible to make direct comparisons with the photochemistry observed with these hydrocarbons. The irradiation of a 1:1.7 × 10^{-6} nitrogen:cyanoacetylene mixture (experiment 5, Table 3) yielded hydrogen cyanide and trace amount of acetonitrile. The high quantum yield for cyanoacetylene loss (2.3) is indicative of a free radical chain reaction. Hydrogen cyanide was formed from the reaction of CN radicals with hydrogen radicals while acetonitrile may be formed from the reaction of CN radicals with CH_3 radicals.

$$HC{\equiv}CCN \xrightarrow{h\nu} H\bullet + \bullet C{\equiv}CCN, \quad (16)$$

$$HC{\equiv}CCN \xrightarrow{h\nu} HC{\equiv}C\bullet + \bullet CN, \quad (17)$$

$$\bullet H + \bullet CN \xrightarrow{M} HCN, \quad (18)$$

$$\bullet CH_3 + \bullet CN \xrightarrow{M} CH_3CN. \quad (19)$$

The high quantum yields for cyanoacetylene loss and hydrogen cyanide formation appear to be in conflict with the proposed photochemical synthesis of cyanoacetylene by irradiation of hydrogen cyanide–acetylene mixtures (Becker and Hong, 1983). This conflict is resolved by the requirement of a 10:1 or greater hydrogen cyanide:acetylene ratio to form cyanoacetylene, a ratio significantly greater than observed in Titan's atmosphere.

Addition of methane to the photolysis mixture (experiment 6, N_2:CH_4:HC_3N 0.98:0.02:1.2 × 10^{-6}) resulted in a decrease in the quantum yield for cyanoacetylene loss from 2.3 to 1.8 (20) while the quantum yield for hydrogen cyanide formation increased from 0.23 to 0.28 (21). The decrease in the QY of HC_3N loss in the presence of methane, explained by the hydrogen abstraction by a C_3N radical from CH_4 to regenerate HC_3N (20), is consistent with the proposal that (16) is the main process in the photodissociation of cyanoacetylene (Clarke and Ferris, 1995; Seki et al., 1996).

$$\bullet C{\equiv}CCN + CH_4 \rightarrow HC{\equiv}CCN + \bullet CH_3, \quad (20)$$

$$\bullet CN + CH_4 \rightarrow HCN + \bullet CH_3. \quad (21)$$

The QY for ethane formation increased from 0.04 to 0.34 and there were smaller increases in the quantum yields for the formation of propane and acetylene (Table 3). The changes in quantum yields of ethane and propane correspond with those observed when methane is mixed with cyanoacetylene indicative of the important role of methane in the formation of higher hydrocarbons on Titan.

Acrylonitrile ($CH_2{=}CHCN$) was observed as a photoproduct when a nitrogen:cyanoacetylene mixture (mixing ratio 1:1.7 × 10^{-4}) was irradiated in a flow reactor (Clarke et al., 2000) but was below GC detection limit when lower mixing ratios of cyanoacetylene were used. Acrylonitrile was also observed as a product of the photolysis of 5:1 mixture of acetylene and hydrogen cyanide (Becker and Hong, 1983). It is possible that very small amounts of acrylonitrile, formed by the action of solar UV, are present in Titan's atmosphere.

3.3. Photolysis of a Titan atmospheric mixture

Irradiation of a Titan atmospheric mixture that contained many of the gases present in Titan's atmosphere (experiment 7, nitrogen:methane:hydrogen:acetylene:ethylene:cyanoacetylene, 0.98:0.018:0.002:4 × 10^{-6}:3 × 10^{-6}:2 × 10^{-7}) gave a low quantum yield for acetylene loss (0.08) compared to the quantum yields for acetylene loss on irradiation of a mixture of nitrogen:acetylene (1.1), nitrogen:acetylene:ethylene (0.73), or nitrogen:acetylene:methane (0.45) (Table 3). These data indicate a cumulative effect of both the methane on the regeneration of acetylene and the formation of acetylene from ethylene, respectively, on the low quantum yield for the loss of acetylene. Since the combined ratios of acetylene and ethylene at 70° north latitude are approximately forty times greater than that of cyanoacetylene it is likely that the products formed in greater amounts will come from the major hydrocarbon precursors (Fig. 2).

Higher molecular weight volatiles were formed by irradiation of a mixture of Titan's atmospheric gases in which the UV light-absorbing compounds (acetylene, ethylene, and cyanoacetylene) had mixing ratios with 100-fold higher amounts than in previous studies to obtain sufficient organics for the GC/MS analysis of minor reaction products. The mixing ratios of nitrogen, methane and hydrogen were maintained at Titan levels (nitrogen:methane:hydrogen:acetylene:ethylene:cyanoacetylene, 0.98:0.018:0.002:4 × 10^{-4}:3 ×

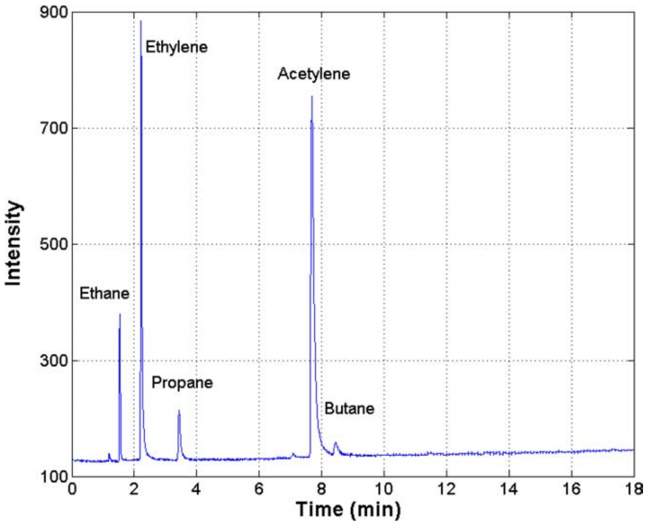


Fig. 2. GC/FID chromatogram of the volatile products from the photolysis of N_2:CH_4:H_2:C_2H_2:C_2H_4:HC_3N ($0.98{:}0.018{:}0.002{:}4 \times 10^{-6}{:}3 \times 10^{-6}{:}2 \times 10^{-7}$) for 4 h in the flow reactor.

$10^{-4}{:}2 \times 10^{-5}$). The compounds in the product mixture were identified by GC/MS. The mass spectrometer was set to detect compounds of mass 35 to 350 amu so only organics with a total of three or more carbon or nitrogen atoms were detected (Table 4).

The principal reaction products were saturated hydrocarbons, olefins and alkynes as expected from our studies on the irradiation of acetylene and ethylene. The principal nitrogen-containing product was acetonitrile. Hydrogen cyanide was not detected because its molecular weight is below 35 amu. Low yields of benzene and substituted benzenes were also observed.

More specific information concerning the compounds generated from acetylene and ethylene was obtained from the photolysis of a gas mixture that contained ^{13}C-labeled acetylene:nitrogen:methane:hydrogen:*^{13}C-acetylene*:ethylene:cyanoacetylene, $0.98{:}0.018{:}0.002{:}3.5 \times 10^{-4}{:}3 \times 10^{-4}{:}1.7 \times 10^{-5}$. The ^{13}C-labeled products were identified by comparison with the mass spectral results of the products obtained by photolysis of a comparable gas mixture above that did not contain ^{13}C-labeled acetylene. The alkanes formed were derived mainly from ethylene and methane as shown by the absence of definitive mass spectral peaks two mass units higher from the incorporation of ^{13}C-acetylene. The reaction pathway leading to saturated hydrocarbons from acetylene must not be important when the acetylene is mixed with other components of Titan's atmosphere. The alkenes, alkynes and aromatics were derived from acetylene, ethylene, and methane as shown by mass peaks for both the labeled and unlabeled derivatives. The yields of longer hydrocarbons containing three or more carbon atoms in flow reactor are believed to proceed via radical combination and addition reactions of free radicals below.

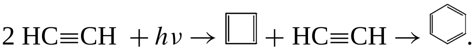
$$\bullet CH_3 + \bullet CH_2CH_3 \xrightarrow{M} CH_3CH_2CH_3, \tag{22}$$

$$HC{\equiv}C\bullet + CH_2{=}CH_2 \rightarrow HC{\equiv}C{-}CH{=}CH_2 + H\bullet, \tag{23}$$

$$2\bullet CH{=}CH_2 \xrightarrow{M} CH_2{=}CH{-}CH{=}CH_2, \tag{24}$$

$$\bullet CH{=}CH_2 + \bullet CH_2CH_3 \xrightarrow{M} CH_2{=}CH{-}CH_2CH_3. \tag{25}$$

The aromatic hydrocarbon products are probably formed by the cycloaddition reactions of acetylene. The mass spectrum of benzene showed the presence of ^{13}C derivatives consistent with the incorporation of up to three labeled acetylenes in the benzene ring (26). It was observed that benzene is one of the products of the photolysis of mixtures of acetylene and cyanoacetylene at 185 and 206 nm (Ferris and Guillemin, 1990). The benzene ring is formed via a cyclobutadiene intermediate that reacts with ground state acetylene to give the benzene ring (26). The substituted benzenes observed in this study are probably formed from the corresponding substituted acetylenes produced by acetylene photolysis.



(26)

Photolysis of mixtures of gases in Titan's atmosphere that contain carbon monoxide remain to be investigated. It is expected that oxygenated organics will be formed as a consequence of the incorporation of carbon monoxide into the solids observed by Clarke and Ferris (1997b).

3.4. Condensation of volatiles

The volatile compounds described in this study are present in the gas phase at 298 K at the atmospheric pressure of the Earth. The volatiles on Titan will be those in the vapor state at the much lower temperatures and pressures on Titan. The variations in the vapor pressure of the organics believed to be present on Titan with atmospheric pressure were previously calculated by Sagan and Thompson (1984) and in a thesis by Guez (1997). The method used by Sagan and Thompson involved a number of approximations. We repeated the calculation of the variation of the vapor pressure with pressure and temperature using experimental data obtained at higher temperatures and pressures (Table 4) (also see Supplementary material) (Boublik et al., 1984). Qualitative but not quantitative agreement was obtained with the results from Sagan's laboratory. These calculations suggest that most of the hydrocarbons containing 6 or more carbon atoms and hydrogen cyanide, acetonitrile and cyanoacetylene will condense on Titan's haze particles at 170–180 K and pressures of 1 mbar or higher to form aerosols. The actual condensation pressure will be higher than calculated because mixtures of compounds will be condensing together which results in a higher saturation vapor pressure (Sagan and Thompson, 1984). Thus the laboratory analogs of Titan's haze will differ from those of Titan haze if they are not formed and analyzed at 170 K because they do not have these volatiles condensed on them. There may be important differences in the optical properties of the haze analogs if they have low molecular weight organics condensed on their surfaces. Vapor pressure–temperature plots for other photoproducts are included with the Supplementary material.

Table 4
The GC/MS analysis of the volatiles obtained from the photolysis of gas mixture containing Titan atmospheric constituents. Molar percentage is calculated among the detected compounds (not including C_2H_6, C_2H_4, and C_2H_2). The GC/MS plot is in the Supplementary material. The calculated vapor pressures of these compounds at 170 K, corresponding to altitude of 200 km above Titan's surface are also given. The plots of vapor pressure with temperature are in Fig. 3 and in the Supplementary material

Peak number	Formula	Tentative identification	Retention (min)	Molar percentage	Vapor pressure (mbar)[a]
1	C_3H_6	Propene	4.84	7.04	2.58E+00
2	C_3H_8	Propane	4.83	75.41	2.24E+01
3	C_4H_{10}	Isobutane	5.27	0.02	2.75E+00
4	C_3H_4	1-Propyne	5.21	0.12	3.79E+00
5	C_4H_8	1-Butene	5.77	0.21	1.49E+00
6	n-C_4H_{10}	*n*-Butane	5.78	8.90	1.12E+00
7	C_4H_6	1,3-Butadiene	5.99	0.05	1.77E+00
8	C_4H_8	*trans*-2-Butene	6.02	<0.01	9.69E−001
9	C_4H_8	*cis*-2-Butene	6.35	<0.01	6.69E−001
10	C_4H_4	1-Buten-3-yne	6.35	0.40	–
11	C_4H_6	1-Butyne	6.55	0.03	3.33E−001
12	C_5H_{10}	3-Methyl-1-butene	7.00	<0.01	2.39E−001
13	C_5H_{12}	Isopentane	7.30	<0.01	1.39E−001
14	C_4H_2	1,3-Butadiyne	7.38	3.39	8.63E−004
15	C_5H_8	3-Methyl-1-butyne	7.88	0.09	–
16	C_5H_{10}	1-Pentene	8.18	0.12	9.29E−002
17	C_5H_{12}	*n*-Pentane	8.28	0.02	6.35E−002
18	HC_3N	Cyanoacetylene	8.36	3.09	2.00E−003[b]
19	C_5H_{10}	*trans*-2-Pentene	8.90	<0.01	4.90E−002
20	C_5H_6	2-Methyl-1-buten-3-yne	8.97	0.01	–
21	C_4H_6	2-Butyne	9.08	<0.01	–
22	C_5H8	Isoprene	9.30	<0.01	–
23	C_5H_{10}	2-Methyl-2-butene	9.30	<0.01	4.11E−002
24	C_5H_{10}	*cis*-2-Pentene	9.50	<0.01	4.27E−002
25	C_5H_{12}	2,2-Dimethylbutane	9.71	<0.01	2.24E−002
26	C_5H_8	1-Pentyne	10.24	0.09	–
27	CH_3CN	Acetonitrile	11.05	0.01	1.46E−003
28	C_5H_8	1,3-Pentadiene (like)	11.63	0.02	2.43E−002
29	C_5H_{10}	4-Methyl-1-pentene	11.38	0.02	–
30	C_5H_{10}	3-Methyl-1-pentene	11.38	0.02	–
31	C_6H_{14}	2,3-Dimethylbutane	11.58	<0.01	9.86E−003
32	C_5H_8	1,3-Pentadiene (like)	11.63	0.01	2.43E−002
33	C_6H_{14}	2-Methylpentane	11.65	<0.01	6.59E−003
34	C_5H_8	Cyclopentene	12.30	0.01	–
35	C_5H_8	2,3-Pentadiene (like)	12.33	0.01	2.43E−002
36	C_5H_{10}	Cyclopentane	12.63	<0.01	2.48E−002
37	C_6H_{14}	3-Methylpentane	12.74	0.01	5.20E−003
38	C_6H_8	1,2,5-Hexatriene	13.20	0.02	1.23E−003
39	C_6H_{10}	3-Methyl-1-pentyne	13.47	0.21	–
40	C_6H_{12}	1-Hexene	13.80	0.09	4.08E−003
41	n-C_6H_{14}	*n*-Hexane	13.95	<0.01	2.31E−003
42	C_6H_{12}	*trans*-2-Hexene	14.78	<0.01	–
43	C_6H_8	3-Hexen-1-yne	15.13	0.05	–
44	C_6H_{12}	*cis*-2-Hexene	15.58	<0.01	–
45	C_7H_{16}	2,4-Dimethylpentane	15.66	<0.01	8.18E−004
46	C_6H_{12}	Methylcyclopentane	16.81	<0.01	2.26E−003
47	C_6H_{10}	1-Hexyne	17.01	0.20	4.49E−004
48	C_6H_{10}	2,4-Hexadiene (like)	18.67	0.05	4.67E−004
49	C_6H_{10}	3-Methyl-1,3-pentadiene	17.22	0.02	–
50	C_7H_{16}	2-Methylhexane	18.49	<0.01	3.00E−004
51	C_6H_{10}	2,4-Hexadiene (like)	18.67	0.09	4.67E−004
52	C_7H_{16}	2,3-Dimethylpentane	18.89	<0.01	3.69E−004
53	C_7H_{16}	3-Methylhexane	19.23	<0.01	2.12E−004
54	C_6H_{12}	Cyclohexane	19.64	<0.01	9.69E−004
55	C_8H_{18}	2,2,4-Trimethylpentane	19.91	<0.01	1.71E−004
56	C_7H_{12}	1,6-Heptadiene	20.63	0.02	–
57	n-C_7H_{14}	*n*-Heptane	21.04	<0.01	3.53E−007
58	C_6H_6	Benzene	21.17	0.02	5.27E−004
59	C_6H_{10}	2-Hexyne	21.32	<0.01	4.49E−004

(*continued on next page*)

Table 4 (*Continued*)

Peak number	Formula	Tentative identification	Retention (min)	Molar percentage	Vapor pressure (mbar)[a]
60	C_7H_{10}	1-Hepten-6-yne	23.56	0.01	–
61	C_7H_{14}	Methylcyclohexane	23.73	<0.01	1.66E−004
62	C_8H_{18}	2,3,4-Trimethylpentane	24.61	<0.01	3.18E−005
63	C_8H_{18}	2-Methylheptane	25.25	<0.01	7.39E−006
64	C_8H_{18}	3-Methylheptane	25.87	<0.01	6.66E−006
65	n-C_8H_{18}	*n*-Octane	27.53	<0.01	2.01E−006
66	C_7H_8	Toluene	28.28	<0.01	4.16E−004
67	C_7H_{14}	Cycloheptane	29.33	<0.01	1.70E−005
68	C_8H_{16}	Ethylcyclohexane	31.02	<0.01	–
69	n-C_9H_{20}	*n*-Nonane	33.39	<0.01	3.86E−008
70	C_8H_{10}	Ethylbenzene	34.19	<0.01	1.38E−006
71	C_8H_{10}	*m*,*p*-Xylene	34.48	<0.01	1.19E−006
72	C_8H_6	Phenylacetylene	35.78	<0.01	–
73	C_8H_{10}	*o*-Xylene	36.17	<0.01	6.49E−007
74	C_8H_8	Styrene	36.20	<0.01	5.02E−007
75	n-$C_{10}H_{22}$	*n*-Decane	38.63	<0.01	5.02E−010
76	C_9H_{12}	1,3,5-Trimethylbenzene	39.66	<0.01	6.88E−009
77	C_9H_{12}	1,2,4-Trimethylbenzene	41.20	<0.01	1.71E−008

[a] Vapor pressure of gases, calculated at 170 K, corresponding to altitude of 200 km above Titan's surface. The data are obtained using Antoine formula: $\log(p) = A - B/(T + C)$ (Boublik et al., 1984).

[b] Data obtained from Benilan et al. (1994).

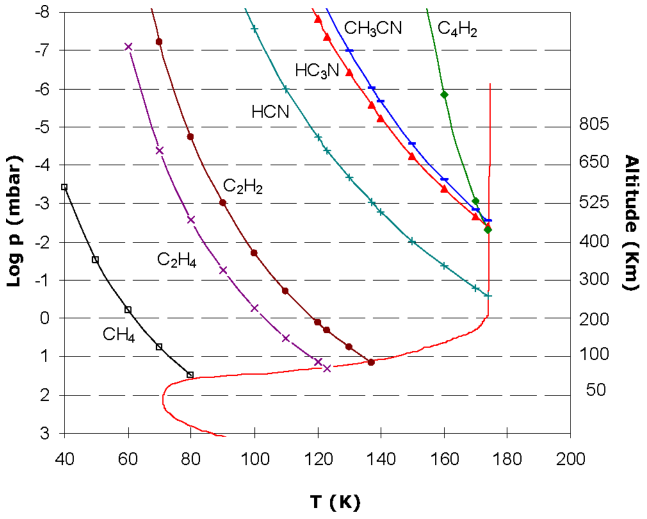


Fig. 3. Vapor saturation temperature profiles for Titan atmospheric mixture including methane, ethylene, acetylene, hydrogen cyanide, cyanoacetylene, and diacetylene. Vapor pressures for other gases are given in Table 4. The data are obtained using Antoine formula: $\log(p) = A - B/(T + C)$ (Boublik et al., 1984) (Table 4). The solid curve is the temperature profile of Titan's atmosphere (Lellouch et al., 1989). The profiles for gases not given in this figure are in the Supplementary material.

3.5. Comparison of photochemical and discharge products

It has not been established which energy source should be used in conducting laboratory studies of the chemical processes in Titan's atmosphere, discharges or UV radiation. Cold plasmas, negative corona and electric arcs have been used to model the action of radiation other than UV light on Titan atmosphere (Ramirez et al., 2001). The cold plasma appears to be accepted by most scientists in the field as the proper energy source for simulating the action of magnetospheric electrons on Titan's atmosphere (Coll et al., 1999a; Imanaka et al., 2004). While it is not possible to determine the most appropriate energy source until data is returned from the Huygens probe, it will be possible to illustrate the differences in the products between these energy sources by comparison of the ten most abundant products formed by different methods (Table 5). The products formed by UV radiation have the closest correlation with those formed by a cold plasma. Saturated and unsaturated hydrocarbons are formed by both energy sources. The difference is that benzene and propionitrile are among the major products formed by the cold plasmas while benzene is a minor product and propionitrile was not detected as a product in the photochemical studies. The negative corona discharge reactions generate saturated organics while the electric discharge reactions yield mainly unsaturated organics. It may be possible to deduce from the amounts of the major compounds on Titan (in the liquid and gas phases) the more important energy source for the formation of organics on Titan.

Discharges dissociate nitrogen gas into very energetic nitrogen atoms that react with species generated from the dissociation of methane to give a high proportion of nitrogen-containing compounds. Long wavelength UV does not dissociate nitrogen gas so the proportion of nitrogen-containing compounds resulting from solar UV radiation will be much lower. This will be an important criterion to differentiate between processes initiated by UV light and those formed by discharges.

There is disagreement whether PAHs are formed in discharge experiments performed to simulate the atmospheric chemistry on Titan. PAHs have been reported in several studies where discharges were used to generate a simulated Titan haze (Imanaka et al., 2004). The upper limit for PAHs containing more than four fused aromatic rings was proposed to be 6% of the mass of the Titan's haze layer (Sagan et al.,

Table 5
Comparison of the ten most abundant volatile reaction products formed by different energy sources in decreasing order of amount[a]

	UV (185, 254 nm)	Cold plasma[b]	Negative Corona[c]	Electric (Arc)[c]
1	Propane	*n*-Butane	*n*-Butane	1-Butene-3-yne
2	*n*-Butane	Propyne	Acetonitrile	Allene
3	Propene	2-Methylpropane	2-Methylbutane	Benzene
4	Butadiyne	Propene	2-Methylpentane	Propane
5	1-Butene-3-yne	*n*-Butane	Propane	Butyne
6	3-Methyl-1-pentyne	Allene	HCN	2-Methyl-1-butene-3-yne
7	1-Butene	Propionitrile	3,3-Dimethylpentane	2-Butyne
8	Propyne	Benzene	2,2-Dimethylpropane	Toluene
9	1-Pentyne	Butadiyne	2-Methylpropane	Cyanogen
10	3-Methyl-1-butyne	2-Methylbutane	Propionitrile	Cyclopentadiene

[a] Two carbon compounds and cyanoacetylene are not shown since they are starting materials in the formation of products by ultraviolet light.
[b] Data from Coll et al. (1999a).
[c] Data from Ramirez et al. (2001).

1993). In another study no aromatic compounds larger than benzene were observed (Coll et al., 1999a). Since polycyclic aromatic hydrocarbons (PAHs) are solids at 25 °C they are not expected to be present in the volatile fraction of the photolysis reaction described previously. A separate search was designed to detect PAHs by extracting them from the flow reactor cell with methylene chloride. The extract was concentrated and analyzed by GC/MS and by HPLC using fluorescence detection. No PAHs were observed. The absence of aromatic compounds containing two or more fused rings in our studies suggests that there are no higher molecular weight PAHs generated by solar UV in Titan's haze.

4. Conclusions

Photolysis of mixtures of gases that simulate Titan's atmosphere results in the formation of reduced forms of organic compounds and little in the way of polyacetylenes and polycyclic aromatic hydrocarbons. This is the consequence of the generation of hydrogen atoms and radicals that add to double and triple bonds. Consequently the gaseous compounds formed are either saturated hydrocarbons or hydrocarbons with a limited number of double and triple bonds. Those hydrocarbons with more than six carbon atoms are expected to be present mainly as aerosols that have condensed on the particles that make up Titan's haze.

Small amounts of simple aromatic compounds are formed and are also expected to be mainly present in aerosols. Our studies suggest the absence of photochemically generated PAHs. We did not detect polyacetylenes longer than diacetylene in our studies. There is the possibility that polyacetylenes longer than diacetylene are formed photochemically but decompose at the temperatures of our reactions (298 K).

The nitriles present in Titan's haze are expected to be mainly hydrogen cyanide, cyanoacetylene, and acetonitrile, compounds that have already been detected in Titan's atmosphere. Low levels of nitrogen-containing compounds are expected because long wavelength UV does not dissociate molecular nitrogen into the reactive nitrogen atoms required to form nitrogen-containing organics. The cyanogen (C_2N_2) and dicyanoacetylene (C_4N_2) present on Titan are probably formed by discharges acting on methane and nitrogen (Coll et al., 1999a, 1999b). The nitriles will be present in the liquid and solid phases on Titan and in smaller amounts in the gas phase.

The structural units observed in the volatile compounds are also expected to be present in the haze particles. The one difference is that the haze material is much higher molecular weight due to polymerization reactions while the volatile fraction consists of organics with fewer double bonds that were not incorporated into polymers. The UV absorption of the haze analogs formed photochemically suggests the presence of double bonds and groups of conjugated double bonds that absorb in the 200–600 nm range (Tran et al., 2003b). The infrared spectrum indicates the presence of double bonds; nitrile groups conjugated with double bonds as well as saturated segments of the polymer as shown by the presence of $–CH_2–$ and $CH_3–$ groups. The C/N ratio in the haze is predicted to be in the 10–20:1 range. As noted above there will be low molecular weight hydrocarbons condensed on the haze particles.

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Supplementary material

The online version of this article contains additional supplementary material.

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