

# The role of photochemistry in Titan's atmospheric chemistry

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## Abstract

Experimental studies were performed to simulate the action of long wavelength solar UV light on Titan's atmosphere. The experiments were carried out in a photochemical flow reactor using a mixture of gases representative of Titan's atmosphere at 70° north latitude (Titan's north pole) in the winter. The solid analog of Titan's haze formed has optical properties comparable to that determined for Titan's haze from modeling Voyager 1 data. Since the optical properties of the haze analogs formed by discharge reactions also have optical properties similar to Titan's haze. It was concluded that the variation in light absorption with wavelength of the haze in the UV–vis spectral region does not vary sufficiently to discriminate between different haze analogs. The C/N ratio of the haze analog prepared by UV radiation is in the 15–20 range while that formed by the action of magnetospheric electrons is in the 2–5 range. The infrared spectrum of the haze analog has absorption bands attributed to CH<sub>3</sub>, CH<sub>2</sub>, C=CC≡N, C=C and possibly N–H groups. The UV spectrum is consistent with the presence of double bonds and conjugated double bonds. No polycyclic aromatic compounds were detected. The volatile photoproducts mainly consist of saturated, olefinic and acetylenic hydrocarbons along with much smaller amounts of benzene and substituted benzenes. Among these volatiles hydrogen cyanide is probably the most abundant nitrogen containing with much less acetonitrile, and trace amounts of acrylonitrile. Some of these volatiles will condense on haze particles at the temperatures and pressures on Titan. The comparison of the volatiles formed by UV radiations are compared with those formed by three different discharges.

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## 1. Introduction

Titan, the largest moon of Saturn is unique among our solar system's satellites in that it has a dense atmosphere that consists mainly of nitrogen (98%) and methane (2%). The atmosphere has layers of haze that are formed mainly by the action of solar ultraviolet (UV) light and Saturn's magnetospheric electrons on the methane and nitrogen in its atmosphere. Titan is also

of interest because there is an ongoing process of the formation of complex organics from nitrogen and methane. Knowledge of the pathways for the formation of complex organics on Titan may provide insight into the processes that led to complex structures that resulted in the origins of life on Earth (Clarke and Ferris, 1997a).

The low temperatures in Titan's atmosphere (~170 K) and the even lower surface temperature (96 K) result in the condensation of organics in Titan's atmosphere and the subsequent "rain out" of complex organics on its surface. It is not clear how long the formation of organics has occurred. If it has proceeded for more than  $40 \times 10^6$  years all the methane in its

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atmosphere would have been consumed. Alternatively, the methane may have been present for a long time as the result of the addition of methane to its atmosphere from an unknown source. One postulate is that methane is present as methane clathrates in the ice below Titan's surface and the methane is released during occasional heating events (Mousis et al., 2002).

The goal of this research is to conduct laboratory studies that provide insight into the chemistry in Titan's atmosphere. In conducting this research, it has not been attempted to simulate the action of all the energy sources and the gradients of pressure and temperature on the predominant nitrogen–methane atmosphere in one laboratory experiment. The approach in the present research is to vary individual parameters with the goal of understanding the principal chemical reactions in the atmosphere. The emphasis in this paper is on the data obtained by the use of ultraviolet light as the energy source. We compare our photochemical findings with those obtained from studies of the action of discharges on methane–nitrogen atmospheres.

## 2. Energy sources

Of the two major energy sources that drive the chemical processes in Titan's atmosphere, solar UV radiation deposits 200 times more energy than do Saturn's magnetospheric electrons (Sagan and Thompson, 1984). This calculation does not include the solar UV in the 80–155 nm wavelength region. The energy deposited by the combination of magnetospheric electrons and UV light of wavelengths less than 80 nm dissociates nitrogen into nitrogen atoms. These very energetic atoms react with similar reactive intermediates formed by the dissociation of methane to generate hydrogen cyanide. The solar UV at wavelengths greater than 80 nm does not dissociate nitrogen, but does initiate other reactions. For example, photolysis of a mixture of hydrogen cyanide and acetylene generates cyanoacetylene (Becker and Hong, 1983).

Light at wavelengths longer than 155 nm is not absorbed by methane so it penetrates down to the cloud tops of Titan and initiates reactions at lower levels of its atmosphere. Since the UV emission from the Sun increases exponentially with wavelength the solar flux is much higher at these longer wavelengths than at the shorter wavelengths. Consequently, we have limited our laboratory studies to an investigation of the products of the action of long wavelength UV light on Titan's atmosphere. A low pressure mercury lamp with emissions at 185 and 254 nm was used as the UV source. The 185 nm radiation is absorbed by acetylene, ethylene and cyanoacetylene, constituents of Titan's atmosphere

and the 254 nm radiation is absorbed by some of their photoproducts.

## 3. The model of Titan's atmosphere

Since discharges were not used in this research to simulate the compounds formed by the action of magnetospheric electrons or the photolysis of methane, we used the composition of Titan's atmosphere at 70° north latitude as the starting point in our photochemical studies (Clarke and Ferris, 1997a; Coustenis et al., 1993). It is assumed that the compounds present at 70° north were formed mainly by magnetospheric electrons since the atmosphere there contains higher proportions of acetylene, ethylene and cyanoacetylene than the atmosphere at the equator because it is shielded from the solar UV. This shielding is a consequence of the tilt of Titan's axis of rotation that limits the amount of sunlight reaching Titan's thick atmosphere at latitudes higher than 70° north during the winter (Clarke and Ferris, 1997a; Yung, 1987). The composition of Titan's atmosphere at 70° north is believed to approximate Titan's atmosphere after bombardment with magnetospheric electrons before it has undergone extensive solar radiation.

## 4. Photochemical flow reactor

A flow reactor (Fig. 1) developed by Clarke et al. (2000) and Tran et al. (2003a) was used in place of a simple quartz cell to avoid these problems. A mixture of reactants with mixing ratios comparable to those present in Titan's atmosphere at 70° north latitude, were flowed past the UV lamp for 50–200 h to generate sufficient

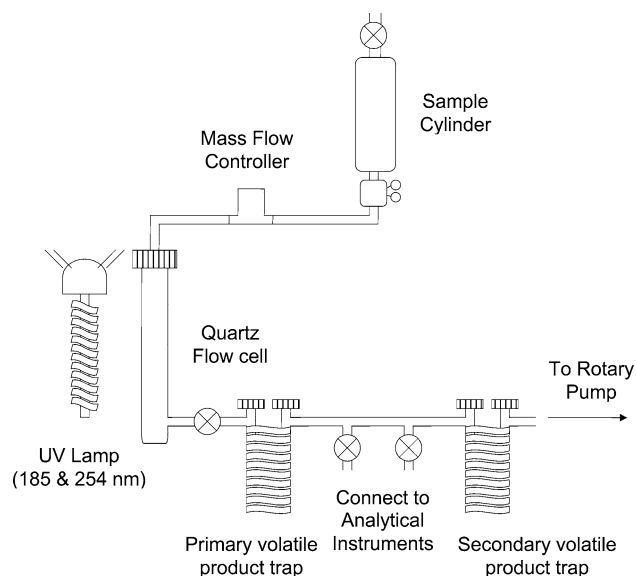


Fig. 1. Schematic diagram of the photochemical flow reactor.

amounts of solid products for spectral and analytical studies. With mixing ratios in the  $10^{-4}$ – $10^{-7}$  of reactants, insignificant amounts of solid product condensed on the wall of the flow reactor. Wall effects were minimized because greater than 99% of the UV passed through the cell. So, the reactions proceeded in the interior of the reactor chamber and not just at the cell walls.

## 5. Simulation of Titan's Haze

The solid products condensed as films on quartz and gold-coated silicon plates placed in the flow reactor (Tran et al., 2003b). The 50 nm thick films deposited on quartz plates were used for the measurement of the UV–visible–near infrared absorption. The real ( $n$ ) and imaginary ( $k$ ) coefficients of the refractive indices of the film were calculated from the light absorption by the films. The elemental composition of the films was determined by X-ray photoelectron spectroscopy measurements on the polymer films deposited on the gold-coated silicon plates (Tran et al., 2003a). The infrared spectra of the polymers were measured on film samples scraped from the silicon plates.

### 5.1. Optical properties of Titan haze analogs

The optical properties of the simulated haze samples prepared from a mixture of nitrogen, methane, hydrogen, acetylene, ethylene and cyanoacetylene (0.98:0.018:0.002: $3.5 \times 10^{-4}$ : $3 \times 10^{-4}$ : $1.7 \times 10^{-5}$ ) are comparable to those prepared by a spark discharge (Khare et al., 1984) or a plasma discharge (Ramirez et al., 2002) with the exception that the magnitude of the  $k$

values for the plasma discharge sample is 10 times lower than the others. The purpose of this study was to determine which haze analog came the closest to fitting the plot ( $k$  versus  $\lambda$ ) in the 200–800 nm wavelength region that was derived from the data obtained by the Voyager 1 spacecraft and was therefore the best model of Titan's atmosphere (Fig. 2). All three samples are comparable to the plots calculated by modeling the data from the Voyager 1 spacecraft (McKay and Toon, 1992; Rages and Pollack, 1983). In these and similar models, it was noted that the magnitude of  $k$  has an error of about 2 while that of the variation of  $k$  with wavelength (slope) had a much lower error (McKay and Toon, 1992; Rages and Pollack, 1983). It is suggested that the slope should be  $\lambda^{-4}$ . The  $k/\lambda$  plots shown in Fig. 2 have slopes that vary from  $\lambda^{-3}$  to  $\lambda^{-5}$  for haze prepared by discharges and UV radiation. It is concluded that the data are not sufficiently precise to distinguish between them by their slopes. An alternative conclusion is that  $k$  values are not sufficiently different in these analogs to use  $k/\lambda$  plots to determine which haze analog provides the best fit to Titan data.

### 5.2. Elemental analysis of the Haze analogs

The elemental analysis of the Titan haze analogs prepared by discharges and UV radiation differ significantly. The C/N ratios reported for samples prepared by discharges are in the 2–5 range while those prepared photochemically are in the 15–20 range (Table 1). In the discharge driven reactions, the dissociation of molecular nitrogen is an ongoing process and that leads to the much higher proportion of nitrogen in the haze

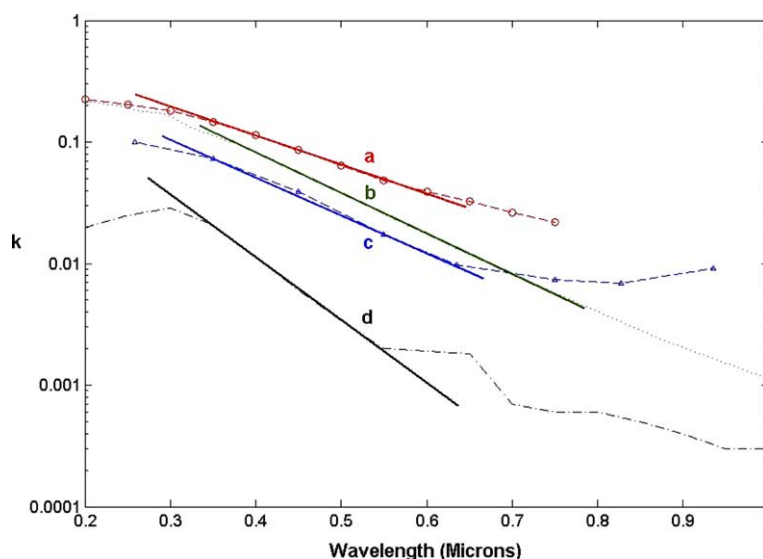


Fig. 2. Variation of the slope of the Titan's haze analogs with wavelength (a) UV photopolymer (slope  $\sim \lambda^{-3}$ ) (Tran et al., 2003b), (b) spark discharge product (slope  $\sim \lambda^{-4}$ ) (Khare et al., 1984), (c) model based on Voyager 1 data (slope  $\sim \lambda^{-3}$ ) (Rages and Pollack, 1980), (d) plasma discharge product (slope  $\sim \lambda^{-5}$ ) (Ramirez et al., 2002).

Table 1  
C/N ratio in Titan haze models

Gas mixture	Energy source	C/N ratio	References
9:1, N <sub>2</sub> :CH <sub>4</sub>	Spark discharges	1.5	McDonald et al. (1994)
9:1, N <sub>2</sub> :CH <sub>4</sub>	Spark discharges	5.5	McKay (1996)
98:2, N <sub>2</sub> :CH <sub>4</sub>	Flow glow discharges	2.8	Coll et al. (1999)
N <sub>2</sub> :CH <sub>4</sub> :H <sub>2</sub> :C <sub>2</sub> H <sub>2</sub> :C <sub>2</sub> H <sub>4</sub> :HC <sub>3</sub> N 0.98:0.018:0.002:3.5 × 10 <sup>-4</sup> :3 × 10 <sup>-4</sup> :1.7 × 10 <sup>-5</sup>	UV at 185 and 254 nm	17.6	Tran et al. (2003a)

analogs in the 2–5 range. Molecular nitrogen is not dissociated by UV wavelengths greater than 80 nm so there are no reactive nitrogen atoms formed by UV light of wavelengths 185 and 254 nm. The nitrogen incorporated into the haze originates from the low levels of cyanoacetylene in the mixture of reactant gases. In unpublished studies, it was found that irradiation of mixtures that contain hydrogen cyanide and cyanoacetylene does not result in the incorporation of nitrogen into the polymeric product. The analytical data returned from the Huygens probe will provide an indication of the principal energy source driving haze formation on Titan. Values of C/N in the 2–5 range are characteristic of magnetospheric electrons while those closer to 15/20 suggest that solar UV is the principal energy source.

### 5.3. Infrared spectra of Haze analogs

The infrared spectra of laboratory haze analogs prepared by the long wavelength UV light exhibit CH<sub>3</sub>, CH<sub>2</sub>, CN and olefin (C=C) absorption bands (Tran et al., 2003a). There may be N–H absorption bands as well. The CH<sub>3</sub> and CH<sub>2</sub> signals are consistent with the presence of saturated hydrocarbon structural units. The strong double bond absorption band suggests that olefins are also present. The UV absorption of the haze analog at longer wavelengths is consistent with the presence of conjugated double bonds [C=C–(C=C)<sub>n</sub>] (Tran et al., 2003b). The infrared frequency of the nitrile group is consistent with it being conjugated to a double bond [C=C–C≡N].

The haze analogs prepared by discharges have different infrared spectra. The sample prepared by the action of a spark discharge (Khare et al., 1984) differs markedly from the ones prepared by cold plasma discharges (Tran et al., 2003b). The infrared spectra of samples prepared by cold plasma discharges have some similarities (Coll et al., 1999; Imanaka et al., 2004). The infrared spectrum of the haze analog prepared by the action of UV radiation also has some similarities to those formed by cold plasma discharges. This is surprising considering the major differences in the C/N ratios between the haze analogs prepared by UV and those prepared using discharges.

### 5.4. Solubility studies of the Haze analogs

Attempts to dissolve the Titan haze analog prepared by UV radiation gave negative results when a range of non-polar, polar and aqueous solvents and solvent mixtures were investigated (Tran et al., 2003b). It is reported that the haze analog prepared using a spark discharge was soluble in water, polar organic solvents and solvents containing nitrile groups (McKay, 1996). The insolubility of the haze analog formed by the action of UV light is consistent with it being a high molecular weight; cross-linked polymer while the discharge product consists of a mixture of lower molecular weight substances (Tran et al., 2003b).

### 5.5. Polycyclic aromatic hydrocarbons

There are some reports of the presence of polycyclic aromatic hydrocarbons (PAHs) in the Titan haze analogs prepared by the action of discharges on gas mixtures that simulate Titan's atmosphere (Imanaka et al., 2004; Khare et al., 2002; Sagan et al., 1993) while another group did not detect them (Coll et al., 1999). No PAHs were detected in the Titan haze analog prepared by using UV radiation when analytical procedures specifically designed to detect these structures were used (Hodgeson et al., 1990; Winberry and Jungclaus, 1999).

## 6. Volatile products

Approximately 130 compounds were collected in the spiral traps cooled with liquid nitrogen (Fig. 1) when a mixture of gases approximating Titan's atmosphere (listed in Section 5.1) was irradiated in the flow reactor. These compounds were identified by combination gas chromatography/mass spectrometry (GC/MS) and the amounts of 80 of them were quantified. These compounds are mainly hydrocarbons that have 3–10 carbon atoms. The principal classes of compounds present include saturated hydrocarbons, olefins and acetylenes. Benzene and substituted benzenes are formed in lower amounts than the other classes of compounds.

Acetonitrile is the main nitrogen-containing product detected but 2-propenenitrile (acrylonitrile) (Clarke

et al., 2000) may be present in trace amounts. It is likely that hydrogen cyanide is formed by the photolysis of cyanoacetylene as well but it was not detected because the GC/MS was set to detect compounds containing three or more carbon and/or nitrogen containing compounds. No additional nitrogen-containing compounds were detected when both hydrogen cyanide and cyanoacetylene were present in the irradiated gas mixture along with other hydrocarbons. Hydrogen cyanide has stronger light absorption at wavelengths below 130 nm (Abrink et al., 1978). However, light in this wavelength region is mainly absorbed by methane, the most abundant organic in Titan's atmosphere. Therefore, hydrogen cyanide absorbs little solar radiation and its main role in the photochemistry in Titan's atmosphere is the formation of cyanoacetylene from acetylene (Huang et al., 1999).

## 7. Reaction pathways

The reaction pathways leading to the volatile photo-products were investigated by irradiation of mixtures of one to three gases with nitrogen (Tran et al., in preparation). It was determined from these studies that the presence of methane in the gas mixture greatly enhances the yield of ethane and other hydrocarbons as photoproducts. The ethane formed as a result of the abstraction of hydrogen atoms from the methane to form methyl radicals, which in turn combine to form ethane (Yung et al., 1984). This catalytic decomposition of methane was previously observed when the photolysis of acetylene and cyanoacetylene was performed in the presence of methane at 185 nm (Clarke and Ferris, 1995; Smith et al., 1999).

Further insight into the reaction pathways was obtained by use of acetylene in which the two carbon atoms were labeled with carbon-13. A mixture of Titan atmospheric gases was irradiated in which carbon-13 acetylene was substituted for the carbon-12 acetylene. The products containing C-13 were detected by mass spectrometry due to the presence of two or more additional mass units in the reaction products. From this research, it was possible to conclude that the saturated hydrocarbons are not formed from acetylene because they did not contain C-13. Ethylene and methane are the sources of these compounds. This conclusion is consistent with the observation that saturated hydrocarbons are the main products formed when a mixture of nitrogen and ethylene was irradiated in the flow reactor. Both C-13 labeled and unlabeled benzene were detected in the product mixture obtained from the gas mixture containing C-13 acetylene. The benzene that did not contain carbon-13 was probably formed by the photochemical conversion of the carbon-12 ethylene present in the gas mixture to acetylene, which in turn was converted to

benzene. Previous studies show that benzene is formed by photolysis of acetylene (Ferris and Guillemin, 1990; Okabe, 1983).

Only trace amounts of diacetylene were observed by the photolysis of gas mixtures where the acetylene was present in mixing ratios of  $10^{-4}$  –  $10^{-6}$ . The low yields of diacetylene suggest that no polyacetylenes were formed because this requires the subsequent reaction of acetylene with the trace amounts of diacetylene formed. It is more likely that the acetylene will react with the much larger amounts of the other reactants in the mixture being irradiated rather than with the diacetylene. While it is recognized that polyacetylenes are not stable under the reaction conditions used in this study (Vanssay et al., 1995; Coll et al., 1999) we believe it is unlikely that they were formed photochemically in this study.

There are important differences in the volatile products formed when UV or discharges are used to drive the chemistry of gas mixtures that simulate Titan's atmosphere. If the 10 most abundant compounds are compared, it is observed that saturated and unsaturated hydrocarbons are the main products formed by the action of UV radiation. It should be noted that hydrogen cyanide would not be detected by our GC/MS analysis. An electric discharge produces benzene, toluene and cyanogen together with unsaturated hydrocarbons in their 10 most abundant compounds while a negative corona discharge produces mainly saturated hydrocarbons along with hydrogen cyanide, acetonitrile, and propionitrile (Ramirez et al., 2001). A cold plasma discharge generates an array of hydrocarbons similar to the top 10 compounds formed by UV radiation with the exception of propionitrile and benzene (Coll et al., 1999). In the analysis of the Huygens data, it is important to keep in mind that volatile compounds at the temperature and pressures on Earth may be condensed to the liquid or solid phase at the lower temperatures in the atmosphere and on the surface of Titan. In an investigation of the vapor pressures of gases on Titan, it is predicted that compounds with five or more carbon atoms will condense on Titan and the most likely point of condensation is on the haze particles (Sagan and Thompson, 1984; Tran et al., in preparation). Thus, the analysis of the haze particles will give results that represent the solid core and well as the volatiles that condensed on it.

## 8. Carbon monoxide

Carbon monoxide (CO) has not been included in most of the simulations to date even though it is present in Titan's atmosphere in amounts comparable to that of acetylene. In an investigation of the photolysis of a mixture of CO with cyanoacetylene in a static system, the

solid formed exhibited a carbonyl band at  $1740\text{ cm}^{-1}$  in its infrared spectrum that was not present when CO was irradiated alone (Clarke and Ferris, 1997b). This finding suggests that Titan's haze may also contain oxygenated organic compounds although the structures of the organics formed will be different than those observed in this study since there were no hydrocarbon reactants present.

Recent studies using a cold plasma discharge on a CO–methane–nitrogen mixture reported the detection of the three membered cyclic compound ethylene oxide (oxirane) as a product (Bernard et al., 2003). There have been no reports of the formation of ethylene oxide by photochemical reactions so this compound is not likely to be formed by the action of solar UV radiation on Titan's atmosphere.

### 9. Connection between Haze and volatiles

The analysis of the volatiles formed in the photochemical reactions provides clues as to the structures present in the haze analogs. Infrared data indicates the haze particles are composed of hydrocarbons consisting of mainly double bonds. The UV absorption suggests the presence of double bonds; some of which are conjugated (Tran et al., 2003b). These data are consistent with the structural units found in the volatile compounds in which there are double bonds and, to a lesser extent, triple bonds. Since it is possible that the haze is formed by the further elongation of the volatile compounds it is reasonable to conclude that the haze is a high molecular weight substance that contains many of the structural elements present in the volatiles.

### 10. Conclusions

It is concluded from these studies on the action of long wavelength solar UV on gas mixtures that simulate Titan's atmosphere that:

1. The volatiles formed in Titan's atmosphere contain saturated hydrocarbons and hydrocarbons with double bonds and triple bonds. Some of these compounds will contain oxygen functional groups as a consequence of CO in the atmosphere. There will be lower levels of nitrogen-containing and aromatic compounds.
2. The principal nitrogen-containing compounds present in the atmosphere are hydrogen cyanide and acetonitrile both of which are also expected to condense on the haze particles.
3. It is not likely that polyacetylenes longer than diacetylene are formed by the action of solar UV on Titan's atmosphere.
4. The volatiles containing five to six carbon atoms or more will condense out of the atmosphere as aerosols. The haze particles provide nucleation sites for the formation of these aerosols.
5. Titan's haze is a high molecular weight polymer with structural units that contain mainly saturated and unsaturated hydrocarbons. The polymer probably has cross-links between its chains.
6. The haze contains low levels of nitrogen with a C/N ratio in the 10–20 and some oxygen. Experiments remain to be performed to determine what oxygen containing organic are formed.
7. PAHs are absent or present in trace amounts in Titan's haze.

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