UV–Vis Light-induced Aging of Titan’s Haze and Ice

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Abstract

The study of the photochemical aging of aerosols is an important tool for understanding Titan’s stratosphere/troposphere composition and evolution, particularly the haze. Laboratory simulations of the photoreactivity of the haze aerosol analogs provide insight into the photochemical evolution of Titan’s atmosphere at and below the haze layers. Here we use experimental simulations to investigate the evolution of the laboratory analogs of these organic aerosols under ultraviolet (UV)–visible (Vis) photons, which make it through the haze layers during their sedimentation process. We present experimental results for the aging of Titan’s aerosol analogs obtained from two dominant nitrogen-containing organics, HC3N and HC5N, under simulated Titan atmospheric conditions (photons and temperature). We report that volatile nitriles condensed on haze particles could be incorporated through photochemistry and provide one such sink mechanism for nitrile compounds. We provide laboratory evidence that the organic aerosols could photochemically evolve during their sedimentation through Titan’s atmosphere.

Key words: astrochemistry – solid state: refractory – methods: laboratory: solid state – planets and satellites: atmospheres – techniques: spectroscopic – ultraviolet: planetary system

1. Introduction

Titan’s aerosols are the final product of complex carbon-nitrile photochemistry occurring in the upper atmosphere (>1000 km; Koskinen et al. 2011; Horst 2017). Ultraviolet (UV) photons, photoelectrons, energetic ions, and magnetospheric electrons induce the dissociation and ionization of N2 and methane leading to the formation of complex organic molecules, including nitriles and hydrocarbons.

Atmospheric gaseous species produced in the upper atmosphere can descend to the cold tropopause (70 K). At this temperature, many species may undergo further reactions to form complex organic molecules and/or condense, forming microscopic ice particles or aerosols (Fulchignoni et al. 2005; Atreya et al. 2006; Vinatier et al. 2007, 2010a, 2010b; Horst 2017). It is thought that these aerosols can be formed by nitriles that have been detected in Titan’s atmosphere (HCN, HNC, HC3N, CH3CN, C2N2, etc.) whose altitude profiles have been determined by spectroscopic observations (Hanel et al. 1981; Kunde et al. 1981; Marten et al. 2002; Coustenis et al. 2010; Moreno et al. 2011; Cordiner et al. 2014).

As mentioned by Tomasko et al. (2005), only 11% of the sunlight incident at the top of Titan’s atmosphere reaches the surface, which means there is little solar energy available for further chemical processing on the surface. We note that above the haze layers at and above 700 km, photochemical destruction of methane occurs that in fact leads to the formation of fast-reacting radicals CH3, CH2, and CH (Atreya et al. 2006). Our recent studies showed that photochemical transformations of aerosols and organic ice can occur even at and below the haze altitudes. In these previous studies, we chose C2N2 and HC3N ices as model systems for condensed aerosols (Gudipati et al. 2013; Couturier-Tamburelli et al. 2014, 2015). We showed that these cyanopolyne ices undergo photopolymerization to form tholin-like materials when irradiated with a broad UV–visible (Vis) lamp with filters that allow only wavelengths >300 nm, similar to solar radiation reaching the lower stratosphere of Titan. Photopolymers that are obtained from condensed ices of nitriles and other organic molecules have similar spectroscopic properties (Bernard et al. 2006; Gautier et al. 2012; Imanaka et al. 2012) to tholins made from gas-phase discharge and can be called “tholins” according to the recent definition given by Horst (2017). Oftentimes, Titan’s haze aerosol particles are referenced to their laboratory counterparts, “tholins,” which are also called “Titan tholins.” So, the word “tholin” is exclusively applicable to the laboratory analogs, not the haze and aerosols that are a part of Titan’s atmosphere.

Our present study focuses on another nitrile molecule of the cyanopolyne family detected in the solid phase in Titan’s atmosphere (Coustenis et al. 1999), HC3N, which could contribute to aerosol formation. Indeed, in Titan’s atmosphere, these nitriles have much greater northern polar enrichment coming from a seasonal effect (Vinatier et al. 2015) than hydrocarbons with similar photochemical lifetimes, and they can distribute between the stratosphere and troposphere (Teanby et al. 2010). Here HC3N is taken as a precursor of monomers that could form ice and photochemically aged aggregate to form aerosols, which can rain down to the surface.

As suggested for the first time by Clarke & Ferris (1997), photopolymerization of nitrile compounds and their incorporation into Titan’s haze particles could provide such a sink mechanism for nitrile compounds, as showed by Teanby et al. (2010). As the sedimentation velocity is very slow, aerosol particles can stay 10 yr in the lower atmosphere (Lavvas et al. 2010; Gudipati et al. 2013) before sedimenting on the surface. Nevertheless, the aerosol particles can be brought more rapidly to the surface by rain washing (Le Gall et al. 2016). However, when they are in the lower stratosphere and troposphere, they receive UV photons at wavelengths >230 nm. Further, the HC3N ices can accrete molecules on their surfaces, of which the most predominant would be
HCN due to its high abundance in Titan’s atmosphere. Indeed, HC$_3$N and HCN are the most dominant nitriles in Titan’s atmosphere and have mixing ratios between 2.95E$^{-8}$ and 9.7E$^{-7}$ for HCN and 3.1E$^{-10}$ and 4.6E$^{-8}$ for HC$_3$N in the stratosphere for different latitudes given by nadir high resolution (Coustenis et al. 2010). Moreover, Tomasko & West (2009) proposed that at lower altitudes in the stratosphere, the aerosols keep growing to larger sizes, possibly by incorporating molecules.

The main gas candidates (in terms of mass flux and altitude of condensation) involved in condensation processes in Titan’s lower stratosphere and troposphere are methane, ethane, and hydrogen cyanide. As previously mentioned, C$_2$H$_2$ and HCN are formed in Titan’s upper atmosphere from the products of N$_2$ and CH$_4$ photolysis, while methane’s origin lies on the surface or subsurface. Due to the different source regions and thermodynamical properties, these gases can condense at different altitude regions (which can overlap); hence, their impact on the observed optical properties could be large. Relying on photochemical models (Yung et al. 1984; Lara et al. 1996; Lebonnois et al. 2001; Hourdin et al. 2004; Wilson & Atreya 2004; Lavvas et al. 2008), HCN and HC$_3$N are expected to condense close to 75–80 km, which correlates well with the first transition altitude detected by Descent Imager/Spectral Radiometer (DISR; Bezard 2014) and HC$_3$N around 75 km (Horst 2017). Based on Horst’s work (Horst 2017), HCN and HC$_3$N are supposed to condense in the lower part of the stratosphere. But in particular cases, like those mentioned in Anderson et al. (2016), at 70° north in early northern spring, detection of first benzene (C$_6$H$_6$) at 148 km, then HC$_3$N at 144 km, and then hydrogen cyanide (HCN) at 136 km in the gas phase indicates slight variations in their condensation (evaporation) temperatures in Titan’s atmosphere. However, condensation altitudes should be taken with caution, since a large cloud containing HCN ice particles was observed in Titan’s southern pole in 2012 May at an altitude of 300 km. Indeed, the presence of HCN particles at this altitude is characteristic of a substantial cooling of Titan’s atmosphere during the winter polar vortex in early 2012 (De kok et al. 2014). Despite the fact that benzene condenses before HC$_3$N and HCN and some hydrocarbons (C$_2$H$_6$, C$_3$H$_8$, C$_2$H$_4$, etc.) condense afterward, in our work, we expect that HC$_3$N condenses first and is subjected to solar photons resulting in photochemical polymerization, and subsequently, HCN accretes on the HC$_3$N ice/polymer. Our experiments give information on what is happening in Titan’s lower atmosphere, which is considered to be the lower part of the stratosphere (<200 km) and the upper part of the troposphere (between 80 and 40 km).

The purpose of this work is to study the aging of the aerosols exposed to UV–Vis radiation (>300 nm) that correspond to the UV solar radiation that could penetrate deeper into Titan’s stratosphere and troposphere (Tomasko et al. 2005; Lavvas et al. 2011). Earlier studies from our laboratories have shown that under these lower-altitude conditions, photopolymerized organic ices occur, as detailed earlier (Gudipati et al. 2013; Couturier-Tamburelli et al. 2014, 2015; Toumi et al. 2016). Moreover, as said in the review of Horst (2017), “analysis of VIMS solar occultation measurements from 250 to 700 km show an aerosol composition variation. It may indicate aerosol aging and/or condensation onto particles as the particles become more aliphatic in character with decreasing altitude (Courtin et al. 2015). Based on the DISR measurements Tomasko et al. (2008) said that below 80 K, the aerosols are a combination of photochemically generated haze and condensed organics.” So, we report laboratory work here in which two predominant Titan molecules, HCN and HC$_3$N, are used to simulate the aerosol photochemical aging, taking HC$_3$N as a photochemical aerosol initiator.

### 2. Experimental Details

Pure cyanoacetylene was synthesized using the method described by Moureu & Bongrand (1920). The HCN is synthesized from the thermal reaction of potassium cyanide (KCN) and an excess of stearic acid (CH$_3$(CH$_2$)$_{16}$COOH) in a primary pumped vacuum line, as described in Gerakines et al. (2004). We purified the HC$_3$N by degassing the product several times with the help of nitrogen and nitrogen-ethanol baths to avoid the presence of volatile impurities. The experimental apparatus is described in Figure 1. HCN and H$_2$CN were vapor-deposited at a rate of 6 × 10$^{-7}$ mol minute$^{-1}$ on a gold-plated copper surface kept at 70 or 90 K. The temperature of this substrate can be varied between 20 and 300 K with the help of a temperature-controlled cold head cryostat (CTI, model 21) within a high vacuum chamber (ca 10$^{-7}$ mbar). Warming of the samples was done at a heating rate of 1 K minute$^{-1}$ using a resistive heater along with a Lakeshore model 331 temperature controller. The spectra were recorded in reflection-absorption (double-absorption) mode using a Fourier transform infrared spectrometer (Nicolet, II Magna System 750) in the mid-infrared region (from 4000 to 650 cm$^{-1}$). Each spectrum is averaged over 100 scans with a resolution of 1 cm$^{-1}$.

Photolysis experiments have been performed using an Osram 200 W high-pressure mercury lamp ($\lambda = 200–2500$ nm with discrete Hg lines in the UV–Vis region between 200 and 600 nm, where most of the photon flux resides). Irradiation at $\lambda > 300$ nm wavelengths is achieved with the same lamp equipped with a UV cutoff filter with an estimated flux of about $2.75 \times 10^{10}$ photons cm$^{-2}$ s$^{-1}$ (Couturier-Tamburelli et al. 2014). After irradiation, each ice sample is slowly warmed up (1 K minute$^{-1}$) to room temperature. While volatile species are evaporated into the vacuum, the refractory organic residue of...
Molecule | \(S_0\rightarrow S_1\) (First Excited Singlet State) Threshold | \(S_0\rightarrow T_1\) (First Excited Triplet State) Threshold | \(S_0\) (Ground State) Dipole Moment
---|---|---|---
Hydrogen Cyanide | \(\sim155\) | \(\sim225\) | 3.02\(^b\), 2.7\(^c\)
Cyanocetylene | 260\(^b\), 267\(^c\), 269\(^c\) | 341\(^c\) | 3.33\(^d\), 3.33\(^e\)

Notes.
\(^a\) Minaev et al. (2004).
\(^b\) Stiles et al. (2003).
\(^c\) Semiempirical INDO/S-SCI (single excitations only) computations as described in Gudipati (1994).
\(^d\) Malisch et al. (2001).
\(^e\) Experimental, summarized in Fischer & Ross (2003); taken from Couturier-Tamburelli et al. (2015).

The photopolymer is retained on the surface of the substrate, which has been cooled again to lower temperatures to take spectroscopic measurements.

### 3. Results

Our goal is to determine if the nitrile molecules could be consumed in solid phase when they are adsorbed on top of the aerosol during their sedimentation in the lower atmosphere. We formed the aerosols by condensation of HCN and HC₃N followed by long UV radiation (\(\lambda > 230\) nm or \(\lambda > 300\) nm) to induce the formation of the residue (tholin-like material) in lower stratosphere and troposphere conditions (\(<300\) km).

#### 3.1. Infrared and UV Measurements

**3.1.1. UV Absorption of HC₃N and HCN**

To understand the photochemical properties of HCN and HC₃N in the condensed phase, it is important to know the spectroscopic data of the gas-phase molecules that are summarized here (Table 1). The HC₃N absorbs at wavelengths >230 nm through either the strong \(S_0 \rightarrow S_1\) transition (Fischer & Ross 2003) or the weak \(S_0 \rightarrow T_1\) transition (Table 1 of Couturier-Tamburelli et al. 2015). Absorption of light by molecules in the condensed phase, like aerosols, can occur at longer wavelengths compared to the isolated molecules (polarizability of the condensed phase, excition interactions, and spin–orbit coupling). Direct photoexcitation from the singlet ground state to triplet excited state is normally forbidden but has been previously seen in the C₂H₂ condensed-phase experiment (Couturier-Tamburelli et al. 2014).

HCN is known to absorb only at wavelengths shorter than 230 nm in either its \(S_0 \rightarrow S_1\) or \(S_0 \rightarrow T_1\) transitions (Malisch et al. 2001; Minaev et al. 2004; Guennoun et al. 2006).

#### 3.1.2. Infrared Spectrum of HCN Ice

The molecule HCN is linear, with four normal vibrational modes that are all infrared-active. X-ray studies showed that the crystalline phase is composed of hydrogen-bonded chains with all molecules oriented in the same direction (Dulmage & Lipscomb 1951). The ice film HCN infrared spectra (Bernstein et al. 1997; Gerakines et al. 2004) are well documented in the literature.

Figure 2 presents the infrared spectrum of pure HCN ice deposited at 20 K. The spectrum has absorption bands at characteristic frequencies, which are tabulated in Table 2. At 20 K in our experiment, HCN displays three vibrational modes (\(\nu_1, \nu_2, \nu_3\)) with frequencies at 3115, 2100, and 822 cm\(^{-1}\), respectively. The prominent absorption at 1620 cm\(^{-1}\) is assigned as the first overtone of the HCN bending mode at 822 cm\(^{-1}\) (Theule et al. 2011).

Pure HCN ice was heated from 20 to 130 K with a heating rate of 1 K minute\(^{-1}\). The spectrum of HCN at 120 K is also presented in Figure 2. Crystallization of pure HCN occurs gradually between 20 and 120 K, with no definitive change in spectral signatures. Both \(\nu_1\) and \(\nu_2\) shift to higher frequency (3127 and 824 cm\(^{-1}\), respectively) and increase in intensity, while \(\nu_3\) shifts to lower frequency above 80 K (2099 cm\(^{-1}\)), likely due to HCN crystallization (Danger et al. 2011). The overtone at 1620 cm\(^{-1}\) shows a similar temperature dependency as \(\nu_3\), shifting to 1617 cm\(^{-1}\) by 80 K. The HCN starts to sublime above 115 K, and therefore no residue is observed at room temperature.

#### 3.1.3. Infrared Spectrum of HC₃N Ice

The infrared spectrum of solid HC₃N at 90 K has already been published (Dello Russo & Khanna 1996; Khanna 2005). Here we present a full infrared spectrum of pure solid HC₃N at a temperature of 20 K for the amorphous phase and 110 K for the crystalline one (Figure 3), along with the vibrational assignments, by comparing with the earlier studies. The molecule HC₃N is linear, belongs to the \(C_{3v}\) group, and has 10 normal modes of vibration, all infrared-active. Four are degenerate (\(\pi\)), and five are nondegenerate (\(\Sigma\)). Among these bands presented in Table 2, the most intense ones are located at 3210 (\(\nu(CH)\), 2267 (\(\nu(C≡N)\)), and 2066 cm\(^{-1}\) (\(\nu(C≡C)\)).

As in the case of HCN, crystalline HC₃N forms a linear chain of hydrogen-bonded molecules (Khanna 2005; Dello Russo & Khanna 1996). Due to the hydrogen bonding, the wavenumber of the \(\nu(CH)\) stretching mode of the ice (3210 cm\(^{-1}\)) is lower compared to the frequency when HC₃N is isolated in rare-gas matrices (3316 cm\(^{-1}\); Guennoun et al. 2003, 2004, 2005b; Pietri et al. 2009).

The amorphous-to-crystalline phase transition of solid HC₃N was monitored by annealing the amorphous ice from 20 K to room temperature. As shown in Figure 3 and on the infrared spectra, the phase transition completes at 110 K at a higher temperature than HCN. As in the case of HCN, HC₃N ice infrared spectra become sharper (narrow line widths) in the crystalline phase (Figure 3). Desorption of HC₃N occurs around 140 K, in agreement with earlier observations (Coupeaud et al. 2008). As shown in Figure 4, HC₃N sublimation starts around 130 K, reaches a maximum around 145 K, and is completed at 150 K. It is important to specify that we did not obtain residue at room temperature from pure HC₃N ice sublimation either.
3.2. Photochemistry of Solid Ice

3.2.1. Photochemistry of Solid HCN Ice

The HCN ice was irradiated at \( \lambda > 230 \) nm for 20 hr at 90 K.
According to the UV spectrum (with no absorption at \( \lambda > 230 \) nm; Table 1), the photolysis performed at \( \lambda > 230 \) nm induces no detectable change in the infrared spectra. We did not obtain residue when we increased the temperature until room temperature. The same results were obtained when the sample was irradiated at \( \lambda > 300 \) nm.

3.2.2. Photochemistry of Solid HC3N Ice

The solid sample was monitored by infrared spectroscopy during the irradiation of pure HC3N ice. After 146 hr of irradiation at \( \lambda > 300 \) nm at 90 K, around 50\% of the HC3N ice is consumed. The evolution of the \( \nu_2 \) stretching band of HC3N located at 2267 cm\(^{-1}\) as a function of time is fitted by a single exponential decay.

### Table 2

Positions and Attributions of Infrared Absorption Bands of HC3N at 90 K and HCN at 90 K

| Ices (Pure crystalline) | Attributions   | Wavenumbers |
|------------------------|----------------|-------------|
|                        |                | T = 20 K  | T = 90 K  |
| HC3N                  | \( \nu_1 \) CH stretching | 3208     | 3210     |
|                        | \( \nu_2+\nu_4 \) | 3139     | 3137     |
|                        | \( \nu_2 \) C≡N stretching | 2266     | 2267     |
|                        | \( \nu_3 \) C≡C stretching | 2066     | 2066     |
|                        | 2\( \nu_5 \) | 1480     | 1484     |
|                        | \( \nu_4 \) C–C stretching | 879     | 883     |
|                        | \( \nu_5 \) C–H bending | 749     | 755     |

| Ices (Pure crystalline) | Attributions   | Wavenumbers |
|------------------------|----------------|-------------|
|                        |                | T = 20 K  | T = 90 K  |
| HCN                    | \( \nu_1 \) CH stretching | 3115     | 3127     |
|                        | \( \nu_2 \) C≡N stretching | 2100     | 2099     |
|                        | 2\( \nu_3 \) | 1620     | 1617     |
|                        | \( \nu_4 \) C–H bending | 822     | 824     |

### Figure 2

Infrared spectra of HCN between 3500 and 1500 cm\(^{-1}\) at 20 K (bottom) and 120 K (top).

### Figure 4

Integrated normalized absorbance of HC3N \( \nu_2 \) mode with temperature (\( \beta = 1 \) K minute\(^{-1}\)) determined by FTIR spectrometry.

### Figure 5

Evolution of the column density of HC3N during irradiation at 90 K. The column density was calculated from the \( \nu_2 \) stretching mode, and the decrease is fitted by a single exponential decay.

### Figure 3

Infrared spectra of HC3N in the 4000–650 region. Red (bottom) is at 20 K (amorphous phase); black (top) is at 110 K (crystalline phase).
residue of HC₃N irradiation performed at λ > 300 nm are compared with other laboratory tholins (C₄N₂ photolysis; CH₄/N₂ gas-phase discharge) and Titan observational data coming from the Cassini CIRS and VIMS spectrometers (Figure 8). Our HC₃N residue spectrum presents common tholin-like aerosol absorption bands, as discussed below (Imanaka et al. 2004, 2012; Coll et al. 2013; Gudipati et al. 2013; Couturier-Tamburelli et al. 2014). We can also observe the presence of intense and broad bands in the vNH stretching region due to the presence of amine functions (∼3340 cm⁻¹), similar to our earlier observations from the HC₅N photopolymerization residue. The 3057 cm⁻¹ band is attributed to –C≡C–H stretching. The position of this band is in very good agreement with the data recorded by the VIMS instrument at 950 km (Figure 8, gray lines). The –CH stretching bands are observed at 2958, 2926, and 2855 cm⁻¹, very close to those obtained with the HC₃N residue. The two bands observed at 2220 (shoulder at 2260 cm⁻¹) and 2114 cm⁻¹ can be attributed to nitrile and isonitrile stretching modes. The position of the nitrile group obtained from HC₅N photolysis is shifted to a lower frequency (2220 cm⁻¹), indicating that the C≡N bond is slightly weaker in this tholin compared to the tholins obtained from UV photochemistry of C₄N₂ (2230 cm⁻¹) or HC₅N (2263 cm⁻¹). The band located around 1540 cm⁻¹ is due to stretching C≡C as observed in C₄N₂ experiments, indicating that aromatic structures are less present in this residue.

### 3.3. Photochemical Aging of Nonvolatile Tholin with Adsorption of Volatiles

#### 3.3.1. Adsorption of Nitriles

The laboratory analogs of Titan’s aerosols (tholins) were obtained as described earlier by photochemistry of HC₃N, which, after warming up, induces the residue formation. During their sedimentation in the lower atmosphere, which takes place for about 10 yr, aerosols can adsorb molecules, like nitriles, onto their surface. For this reason, we simulated a similar situation in the laboratory by condensing volatile nitriles on the HC₃N photopolymer tholin.

Adsorption of HCN and HC₅N on the nonvolatile tholin: At first, we studied the adsorption of HCN. We deposited HC₅N onto the tholins cooled at 90 K. The HC₃N adsorption at 90 K on the residue surface induces small changes in the stretching CH and CN positions of HC₃N (∼4 cm⁻¹), indicating that no major interaction between tholins and HC₅N exists. Similarly, HCN adsorption at 90 K on the HC₅N tholin’s surface induces small changes in the stretching CH and CN infrared band positions of HCN (∼3 cm⁻¹), indicating that small interactions between tholins and HCN exist, as in the case of HC₃N. It is not surprising, since tholins have CN group, which can interact with the CH of HCN. We chose HCN because it is observed to be highly abundant in Titan’s atmosphere.

Desorption of HCN and HC₅N from the nonvolatile tholin. We followed desorption of HCN deposited on the HC₃N tholin as shown in Figure 9 (bottom), where we plot the υCH-integrated band intensity changes with temperature. Below 115 K, the peak intensity is quasi-unchanged, which is indicative of a stable adsorption state. At 120 K, we observe an abrupt decrease in intensity resulting from the sublimation of solid HCN. The desorption temperature has been measured to be around 125 K (Figure 9, bottom). The HCN desorption follows a zeroth-order kinetic model (Ostwald 1887). To
determine the desorption energy of HCN, we performed a thermal programmed desorption (TPD) study where approximately \(1 \times 10^{17}\) molecules were deposited for each experiment.

The evolution of the number of molecules for a zeroth-order kinetic is given by

\[
-\frac{dN(T)}{dt} = k(T),
\]

where \(N(T)\) is the number of molecules and \(k(T)\) is the temperature-dependent kinetic rate of the considered reaction (here desorption). By applying Arrhenius’s law (Arrhenius 1889) and integrating with time, we have

\[
N(T) = N_0 - \nu_0 \times \exp\left(-\frac{E_{\text{des}}}{RT}\right) \times t.
\]

If we consider the fact that the temperature follows a linear increase \((T = T_0 + \beta t)\), substituting for time \((t)\), the above equation becomes

\[
N(T) = N_0 - \nu_0 \times \exp\left(-\frac{E_{\text{des}}}{RT}\right) \times \left(\frac{T - T_0}{\beta}\right),
\]

where \(T_0\) and \(\beta\) are the initial temperature and heating rates, respectively; \(\nu_0\) is the zeroth-order pre-exponential term; \(E_{\text{des}}\) is the desorption energy; and \(R\) is the ideal gas constant.
The first part of the desorption curves obtained from the infrared signals is fitted to the following expression:

$$\Theta(T) = \frac{N(T)}{N_0(T)} = 1 - \nu_0 \times \frac{T - T_0}{T_\beta} \times \exp\left(-\frac{E_{des}}{RT}\right),$$

where $\Theta(T)$ is the surface coverage (relative integrated absorbance of the $\nu_4$ band) of the solid-phase molecules at the temperature $T$.

For normalization, the first-order pre-exponential term ($10^{13} \text{ s}^{-1}$) is multiplied by $10^{22} \text{ molecules cm}^{-2} \text{ and 1 cm}^2$ factors to respect the dimensions in the surface coverage formula and to give the zeroth-order pre-exponential term, $\nu_0$. If we fix this value to $10^{28} \text{ molecules cm}^{-2} \text{ s}^{-1}$, we obtain $E_{des} = 34.33 \pm 0.79 \text{ kJ mol}^{-1}$ by averaging the different results of each TPD experiment, and the $\pm 0.79 \text{ kJ mol}^{-1}$ uncertainty is the result of the dispersion of $E_{des}$ from the different TPD experiments (Acharyya et al. 2007; Noble et al. 2012a, 2012b). This value is very important, since HCN is one of the major components of Titan’s atmosphere and could be included in astrochemistry codes leading to the residence time ($t_{res}$) of a molecule deposited on the aerosol.

For comparison, we determine the desorption energy of HCN ice deposited on the gold-plated copper surface at 33.11 ($\pm 0.80$) kJ mol$^{-1}$, so the desorption energies are the same whatever the substrate (Figure 9, top).

We use the same methodology to determine the $E_{des}$ of HC$_3$N. We obtain $E_{des} = 38.11 \pm 0.58$ kJ mol$^{-1}$ by averaging the different results of each TPD experiment, and the $\pm 0.58$ kJ mol$^{-1}$ uncertainty is the result of the dispersion of $E_{des}$ from the different TPD experiments.

These $E_{des}$ values are very close to those evaluated for acrylonitrile and propionitrile (Toumi et al. 2016; Couturier-Tamburelli et al. 2018) but lower than that evaluated with TPD for C$_3$N$_2$, 42 ($\pm 5$) kJ mol$^{-1}$ (Guennoun et al. 2005a).

### 3.3.2. Photochemistry of Adsorbed Nitriles on HC$_3$N Tholin

We subjected our HC$_3$N photopolymer tholin (at 90 K) to irradiation at wavelengths greater than 300 nm for 60 hr and found in our experimental conditions no detectable change on the infrared spectrum, indicating no important photochemical aging of nonvolatile HC$_3$N tholin on itself (Figure 12, top). Subsequently, we deposited HCN and HC$_3$N (one at a time for an experiment) and subjected them to irradiation ($\lambda > 300$ nm). These results are described in detail below.

**Photochemistry of HC$_3$N on HC$_3$N photopolymer tholin.** After irradiation of HC$_3$N coated on the residue at $\lambda > 300$ nm for 60 hr, infrared spectra showed a depletion of around 50% of HC$_3$N. Subsequent to warm-up to room temperature after HC$_3$N sublimation, we observed only the increase of intensity of the HC$_3$N photopolymer tholin absorption. We essentially synthesized a second layer of HC$_3$N residue on top of the first one during this experiment.

**Photochemistry of HCN on HC$_3$N photopolymer tholin.** We performed two kinds of experiment, called case 1 and case 2 (Figure 10). Case 1 corresponds to the deposition of HCN on the residue, and then irradiation is made with >300 nm. Case 2 corresponds to irradiation of the residue first for 5 hr with >300 nm and subsequent deposition of HCN without further irradiation. In Case 2, we expect the activated polymer to react with HCN.

1. Case 1

First, irradiation of HCN coated on the residue was conducted at $\lambda > 300$ nm (Table 3). So, as illustrated in Figure 10, both HCN and the residue were photolyzed. Small modifications are observed on the HCN, as well as on the aerosol. We found that HCN deposited on the HC$_3$N nonvolatile polymeric material underwent depletion when it was exposed to longer-wavelength photons (>300 nm). We observed the decrease of the HCN absorption bands (Figure 11) and the small depletion of the 2220 cm$^{-1}$ residue’s band (Figure 12). This result is very interesting, since no modification in our experimental conditions was clearly observed by the irradiation at $\lambda > 300$ nm of the HC$_3$N photopolymer tholin, and the HCN ice is photochemically inert at this wavelength.

When the HCN adsorbed on tholins was subjected to irradiation at $\lambda > 230$ nm, we observed the decrease of the HCN absorption bands and the depletion of the 2260 cm$^{-1}$ (shoulder in the rCN band) tholin band. After 2 hr of irradiation at $\lambda > 230$ nm, around 10% of HCN was consumed. The HCN depletion could indicate several possibilities, including photodesorption, but when the nonvolatile residue was examined spectroscopically, we found a small increase in the CH and CN absorption. Based on CN absorbance of the HC$_3$N photopolymer tholin after and before HCN photochemistry, the incorporated HCN can be roughly estimated as 2%.

During the warm-up under vacuum, after sublimation of HCN, we observed a modification of the spectral feature of the nonvolatile photopolymer. The residue is always orange-brown in color and soluble in methanol. When we compared the differences between the HC$_3$N photopolymer tholin spectrum before adsorption of HCN and after the photolysis experiment, we observed some modifications (Figure 12, bottom). Thus, the infrared bands of the HC$_3$N photopolymer tholin have been slightly modified. In the subtraction spectrum between the residue obtained after the HCN photolysis experiment and before it, we observed the growth of the bands in the CH area (2900 cm$^{-1}$). It is important to note that the bands are located in the aliphatic area and can be due to the aliphatic CH$_3$, aliphatic CH$_2$, and tertiary CH. Another modification observed on the spectrum is the decrease of the 2260 cm$^{-1}$ band in favor of that at 2200 cm$^{-1}$. These bands have been previously attributed to rCN. The band at 2200 cm$^{-1}$ probably corresponds to more saturated nitrile than that at 2260 cm$^{-1}$. This is
indicative of a more conjugated residue. Another effect is the increase of the 1600 cm\(^{-1}\) band corresponding to \(\nu_C=N\) or \(\nu_C=C\). This fact could be interpreted by the progressive vanishing of triple bonds compared to double bonds in the residue.

The increasing CH stretching seen between 3000 and 2900 cm\(^{-1}\) after the photolysis of the HCN deposited on top of the tholins is probably due to the incorporation of hydrogen atoms (\(^\bullet\)H) into the polymer.

### 2. Case 2

As previously explained, the photochemistry of the residue alone at \(\lambda > 300\) nm induces no clear modification in our experimental conditions on its infrared spectrum. Nevertheless, when we coated the residue photolyzed during several hours by HCN (Table 3), we did observe some modifications. (In case 2, only the residue is photolyzed before the HCN adsorption (Figure 10).) After 330 minutes at 90 K, we observed a depletion of HCN of around 10%. Thus, we were not able to detect new product or clear modifications, but we could observe a decrease of the HCN band. This was accompanied by a decrease of the 2220 cm\(^{-1}\) tholin band. Moreover, when we increased the temperature to room temperature, a slight modification of the infrared spectrum of the HC\(_3\)N photopolymer tholin was observed (Figure 12, top). On the subtraction spectrum at room temperature between the residue spectrum before photolysis and after the HCN deposition, we can see the small growth of a CN band located at 2180 cm\(^{-1}\) correlated with the increase of the amine band and, to a lesser extent, the stretching CH. The band at 2180 cm\(^{-1}\) is indicative of a more conjugated polymer compared to the previous one.

### Table 3

Summary of the Actions Performed in the Two Experiments Called Case 1 and Case 2 on the HC\(_3\)N Photopolymer Tholin and the HCN Coated on the HC\(_3\)N Photopolymer Tholin

| Case   | HC\(_3\)N Photopolymer Tholin Irradiation | HCN Deposition | HCN Coated on the HC\(_3\)N Photopolymer Tholin | Irradiation |
|--------|------------------------------------------|----------------|-----------------------------------------------|-------------|
| Case 1 | no                                       | yes            | yes                                           |             |
| Case 2 | yes                                      | yes            | no                                            |             |

![Figure 11](image1.png)

**Figure 11.** Subtraction spectra obtained after 240 minutes (bottom), 60 minutes (middle), and 10 minutes (top) of irradiation at \(\lambda > 300\) nm. Negative absorbance with respect to the baseline (here at 0.004) means depletion of the HCN bands. Positive absorbance is due to the appearance of polymeric material.

![Figure 12](image2.png)

**Figure 12.** Top: subtraction spectrum at 300 K between the end and the beginning of irradiation at \(\lambda > 300\) nm of the HC\(_3\)N photopolymer. Bottom: in case 1, both the HCN and the HC\(_3\)N photopolymer are photolyzed; in case 2, only the HC\(_3\)N photopolymer is photolyzed before the HCN deposition. The two spectra correspond to a subtraction spectrum at 300 K between the end and the beginning of irradiation at \(\lambda > 300\) nm of HCN deposited on top of the HC\(_3\)N photopolymer.

### 4. Discussion

Our focus is to determine if the nitriles could be consumed in solid phase when they are adsorbed on top of the aerosol and subjected to longer-wavelength UV irradiation. Recently, Teanby et al. (2010) determined the relative polar enrichment ratio (70°N/0°N) as a function of the photochemical lifetime of hydrocarbons and nitrile species (see Figure 8 in Teanby et al. 2010). They showed evidence that nitriles are in significantly higher abundances than hydrocarbons with similar predicted photochemical lifetimes. The authors proposed that current models are perhaps missing some loss process for nitriles, and an additional sink term is required that could be due to haze formation or lower-atmosphere photopolymerization of nitrogen species.

Using HC\(_3\)N, one of the nitriles detected in solid phase in Titan’s atmosphere (Samuelson et al. 2007; Anderson...
et al. 2010; Anderson & Samuelson 2011), and one of the most abundant molecules, HCN, we conducted experiments in order to understand the photochemistry of Titan’s condensed aerosols at lower altitude, where the low-energy photons arrive. Some experiments were performed with other cyanopolyynes, like C$_3$N$_2$ and HC$_3$N (Gudipati et al. 2013; Couturier-Tamburelli et al. 2014, 2015). Based on these previous works, here we suggest that lower atmospheric haze analogs may be formed by a contribution of HC$_3$N photolysis. From the fluxes used in the laboratory of $\sim$15 mW cm$^{-2}$ ($\sim$2.75 $\times$ 10$^{15}$ photons cm$^{-2}$ s$^{-1}$) and irradiation time of 146 hr that resulted in 50% depletion of the original HC$_3$N ice, we estimate ice photochemistry forming polymeric nonvolatile tholins involving polar nitriles to be significant and very similar to the nonpolar counterparts that we studied earlier (Gudipati et al. 2013; Couturier-Tamburelli et al. 2014). We estimated earlier that the photon flux on Titan (200–350 nm) was $\sim$10$^{-14}$ photons cm$^{-2}$ s$^{-1}$ or $\sim$70 $\mu$W cm$^{-2}$, about 300 times less than that used in our experiments. So, the photolysis time for 50% depletion of HC$_3$N corresponds to a lower limit of about 5 Earth yr on Titan.

A comparison between laboratory and Cassini observational data from Titan also suggests the presence of HCN (Mayo & Samuelson 2005) condensates. In this work, we have shown laboratory evidence that when aerosols are formed, they can evolve and photochemically age further subsequent to the adsorption of HCN.

Our qualitative and quantitative experiments on haze formation and evolution under UV irradiation conditions led us to estimate the residence times of HCN deposited on the aerosols, which are given in Table 4. We found that this time varies between 4.4 $\times$ 10$^3$ yr at 70 K and 35 yr at 90 K (temperatures characteristic of Titan’s lower stratosphere). Thereby, these times are sufficiently long to photolyze HCN before sedimentation on the surface. This molecule could be subjected to long UV (\(\lambda > 300\) nm) irradiation when it is trapped in/on the aerosols in Titan’s lower atmosphere. As previously mentioned, the laboratory dose is typically 300 times higher than the one received by Titan’s atmosphere at these wavelengths. So, in Titan’s atmosphere, the loss of 10% of HCN could occur within 1 yr.

At these temperatures included between 70 K (for the coolest) and 95 K (temperature of the surface), we demonstrate that HCN desorbs between 35 and 10$^3$ yr, approximately. So, when HCN is formed in the gas phase in the upper part of the atmosphere, it could condense in the lower stratosphere and be accreted onto the aerosol. It is known that when the species are formed, they descend from the upper atmosphere region ($\sim$1000 km) to the cold (70 K) tropopause ($\sim$40 km), and most species are removed by condensation and photodissociation. Thus, HCN, under long UV irradiation, could be incorporated into haze particles and provide one such sink mechanism for HCN compounds. Moreover, this incorporation induces a modification of the HC$_3$N photopolymer tholin, highlighting that the aerosols evolve during their sedimentation.

Teanby et al. (2010) discussed that current models are perhaps missing some loss processes for HCN. As we find photochemical removal of HCN on the HC$_3$N photopolymer tholin, it would be interesting to take into consideration in the atmospheric models the impact of photochemistry in the condensed phase for nitriles.

Coutin et al. (2015) mentioned that when haze particles are descending through the atmosphere, Titan’s atmospheric aerosols lose many of their double bonds by opening them to form bonds with adjacent chains. The authors said that below 480 km, the coating of the aerosols by the available condensable gases is possible. They conclude that as we move down in Titan’s atmosphere, we should see less aromatics and more aliphatics, as shown by the VIMS spectra. Nevertheless, below 300 km, no chemical evolution has been measured clearly by CIRS. The authors conclude that the chemical aerosol rate is much slower than the dynamics. Though no chemical evolution has been measured clearly by CIRS below 300 km (Anderson & Samuelson, 2011), during the photochemical evolution of the coated nitrile residue (in Titan’s simulated lower atmosphere), we observe a small growth of aliphatic CH (as evident from the spectra shown in Figure 12). It is likely that this phenomenon can occur in Titan’s atmosphere (below 300 km), but our signals are too small to warrant searching for in the CIRS data.

### 5. Conclusion

The chemical composition of Titan’s haze is poorly understood; thus, we have conducted a laboratory study in order to contribute to better knowledge of what can happen on Titan, especially in the lower stratosphere and troposphere. We provide evidence that nitriles could be consumed in solid phase both in aerosol formation and in adsorption on the aerosol surface. We propose a new loss process for nitriles in the lower stratosphere and troposphere.

Experimental data presented here show that solar radiation arriving in Titan’s lower stratosphere and troposphere could either (i) initiate tholin-like haze production from the condensation of nitriles at these altitudes or (ii) induce their photochemical aging when molecules are coated onto their surface.

Using HCN as a model molecule (adsorbed on tholin-like haze from the condensation of HC$_3$N), we report evidence that the lower stratosphere and troposphere of Titan is photochemically active. We found that HCN infrared bands depleted upon irradiation and a small amount of new absorption bands were detected, indicating consumption of HCN when it is adsorbed on the aerosols. It is likely that such a mechanism is still operating in the lower atmosphere (stratosphere and troposphere) so that nitriles including HCN could be consumed in solid phase in Titan’s lower atmosphere.

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