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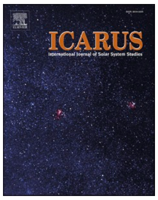

The Titan Haze Simulation (THS) experiment on COSmIC. Part III. XANES study of laboratory analogs of Titan tholins

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ABSTRACT

We have used the Titan Haze Simulation (THS) experimental set-up at NASA Ames' COSmIC facility to produce four laboratory analogs of Titan's aerosols, or tholins. These tholin samples were produced from four gas mixtures of initial compositions N_2:CH_4 (90:10 and 95:5) and N_2:CH_4:C_2H_2 (89.5:10:0.5 and 94.5:5:0.5) at 150 K, using a plasma discharge in the stream of a jet-cooled gas expansion. Here we present an ex situ X-ray absorption near-edge structure (XANES) spectroscopy analysis of these four tholin samples. The C- and N-XANES spectra show the presence of various functional groups (aromatic carbon, imines, nitriles, etc.) whose abundances are correlated with (i) the relative proportions between N_2 and CH_4, and (ii) the presence or absence of C_2H_2 in the initial mixtures. In particular, mixtures containing C_2H_2 result in the formation of tholins consisting of more aromatic structures and displaying larger relative amounts of imines and nitriles, but lower overall nitrogen content. XANES spectroscopy also allowed for the determination of the elemental C/N ratios for the four tholins, which were all found to be low (< 2.5) and consistent with those measured for tholins produced in other, independent experimental set-ups. The C/N ratios of tholins produced from gas mixtures that contained C_2H_2 (2.2–2.4) were found to be about twice as large as those of tholins produced from gas mixtures that did not contain C_2H_2 (0.9–1.3). These new results from the COSmIC/THS experimental set-up demonstrate the impact initial precursors have on the nitrogen chemistry during the formation of tholins, which may help in the interpretation of observations and the development of models of Titan's atmosphere.

1. Introduction

Titan, the largest moon of Saturn, is the only other object in the Solar System besides Earth that possesses a dense atmosphere (1.5 bar at the surface) whose composition is dominated by molecular nitrogen (N_2; 95–98%), with methane (CH_4; 2–5%) as the second most abundant gas (Hanel et al., 1981; Strobel and Shemansky, 1982; Lindal et al., 1983; Fulchignoni et al., 2005; Niemann et al., 2010). A complex organic chemistry between N_2 and CH_4, induced by solar ultraviolet (UV) photons and energetic particles, results in the formation of a large variety of organic compounds that include hydrocarbons such as acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propyne (C_3H_4; also called methylacetylene), benzene (C_6H_6), nitriles such as hydrogen cyanide (HCN), hydrogen isocyanide (HNC), cyanoacetylene (HC_3N), acetonitrile (CH_3CN), ethyl cyanide (C_2H_5CN), and cyanogen (C_2N_2), together with larger, more complex molecules that are believed to include propane (C_3H_8), butane (C_4H_{10}), as well as polycyclic aromatic and heteroaromatic hydrocarbons (see Hörst, 2017; Barnes et al., 2021; and references therein for a complete review).

This complex organic chemistry taking place in the atmosphere also leads to the production of solid particles that form haze layers and play an important role in Titan's atmospheric dynamics, climate, as well as surface composition and processes. Because of its N_2-based dense atmosphere and its CH_4 cycle that resembles the hydrological cycle on Earth, Titan is often compared to the early Earth (Trainer et al., 2004; Lunine and Atreya, 2008; Roe, 2012; He and Smith, 2014). In recent years, Titan's atmosphere and surface were monitored in detail by the NASA *Cassini* mission, which orbited the Saturnian system from 2004 to

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2017 (Matson et al., 2002, 2003; Mitchell, 2006), as well as the ESA *Huygens* probe, which plunged into Titan's atmosphere and landed on its surface in 2005 (Lebreton et al., 2005; Owen, 2005; Zarnecki et al., 2005).

Many laboratory studies have simulated Titan's organic atmospheric chemistry in the past four decades, using various energy sources to induce the dissociation and ionization of N_2 and CH_4. These experiments result in the formation of refractory organic materials that are analogs of Titan's aerosols, often referred to as 'tholins' (Sagan and Khare, 1979; Cable et al., 2012; Coll et al., 2013; He et al., 2017; Hörst, 2017; Sciamma-O'Brien et al., 2017; Sebree et al., 2018). Tholins have been studied using a wide variety of techniques to determine their chemical compositions as well as their physical, chemical, and optical properties (e.g., Cable et al., 2012; Raulin et al., 2012; Brassé et al., 2015; Maillard et al., 2021; Schulz et al., 2021; and references therein). Among other findings, these studies have shown that tholins are macromolecular materials consisting mainly of carbon, nitrogen, and hydrogen, distributed among a mixture of aliphatic and aromatic structures.

In the present study, we produced tholins using the Titan Haze Simulation (THS) experimental set-up at NASA Ames' COsmic SImulation Chamber (COSmIC) facility from four initial gas mixtures that contained mainly N_2, together with 5% or 10% of CH_4, with or without the addition of 0.5% of C_2H_2 (see Section 2.1). We then analyzed these tholins ex situ using X-ray absorption near-edge structure (XANES) spectroscopy to obtain information on their chemical compositions and elemental C/N ratios. After describing the experimental protocol and analytical technique to produce and analyze our tholin samples, we compare our findings with those derived for tholins produced in other, independent experimental studies. Finally, we also describe how these new experimental results may have implications for the interpretation of observational data of Titan's atmosphere, especially during seasonal changes that result in the modification of the relative abundances of specific species.

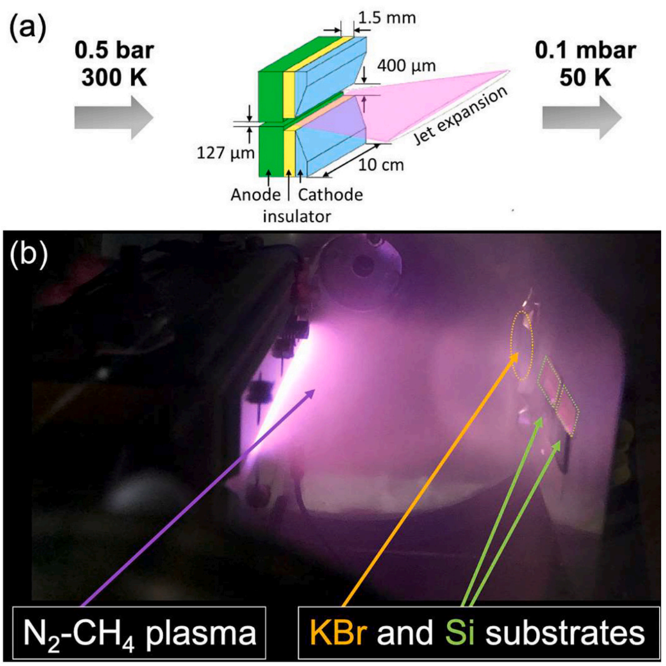

Fig. 1. (a) Schematic of the COSmIC/THS adiabatic expansion of the gas allowing to achieve low temperatures and pressures that are representative of cold atmospheres such as that of Titan (from Broks et al., 2005). The plasma discharge is the energy source used to induce the chemistry in the expansion, by simulating the chemistry induced by charged particles in planetary atmospheres. (b) Photograph of the plasma expansion in the COSmIC/THS chamber during the production of Titan tholins and their deposition on different substrates. Si_3N_4 substrates were used for the experiments reported here.

2. Experimental methods

2.1. *Production of tholins with COSmIC/THS*

Tholin samples were produced using the COSmIC/THS experimental set-up, whose mode of operation has been described in detail in previous publications (Sciamma-O'Brien et al., 2014, 2017; Salama et al., 2018). Briefly, a supersonic, adiabatic expansion is used to (i) cool down a gas mixture, flowing at 2000 standard cubic centimeters per minute (sccm), to Titan-like temperatures (150 K), and (ii) decrease the gas pressure to 30 mbar (Broks et al., 2005; Biennier et al., 2006). A plasma discharge (typically, −700 to −1000 V) generated in the stream of that expansion is then used as an energy source to induce chemistry between the different molecular species present in the jet-cooled gas mixture (Sciamma-O'Brien et al., 2014), hence simulating the electron bombardment of Titan's atmosphere when passing through Saturn's magnetosphere. Although Titan's atmospheric chemistry is induced by both photolysis and radiolysis, it is experimentally advantageous to use a plasma discharge as the energy source instead of a UV lamp, as it enables the dissociation of N_2, hence simulating the nitrogen chemistry taking place in Titan's atmosphere.

Resulting from this chemistry, larger species are formed in the gas phase, eventually leading to the formation of solid particles that can be jet-deposited onto substrates placed in the stream of the expansion. These solid particles, or tholins, are considered analogs of Titan's aerosols, which result from similar processes occurring in Titan's upper atmosphere. Fig. 1 shows (a) a schematic of the pulsed discharge nozzle, which is at the core of the COSmIC/THS chamber and is used to generate the pulsed planar plasma expansion (adapted from Broks et al., 2005), and (b) a photograph of the COSmIC/THS pink N_2-based plasma expansion during solid sample production (note: this picture shows an experiment in which a KBr window and two silicon wafers placed 5 cm from the slit were used as substrates for the deposition). Previous studies have demonstrated the effect of different gaseous precursors present in the initial gas mixture on the formation of both gas-phase (Sciamma-O'Brien et al., 2014; Raymond et al., 2018) and solid-phase (Sciamma-O'Brien et al., 2017) products in the COSmIC/THS chamber, particularly in the cases where acetylene (C_2H_2) is added to N_2:CH_4 gas mixtures, which are traditionally used to simulate Titan's atmospheric chemistry.

In the present study, tholins were produced from four different gas mixtures, namely, N_2:CH_4 (90:10), N_2:CH_4:C_2H_2 (89.5:10:0.5), N_2:CH_4 (95:5), and N_2:CH_4:C_2H_2 (94.5:5:0.5). The abundances of CH_4 relative to N_2 in the gas mixtures chosen for our experiments are representative of the upper limit or higher than the relative CH_4 abundance observed with *Cassini* and *Huygens* instruments as well as ground-based and space observatories (Hörst, 2017, and references therein). Nevertheless, studying these gas mixtures present a couple of advantages: (i) these gas mixtures have been used extensively in previous laboratory studies to simulate Titan's atmosphere, and the results obtained here can therefore be compared with a large number of other experiments, including those performed in our laboratory (Sciamma-O'Brien et al., 2014, 2017), and (ii) due to the truncated chemistry occurring in our experimental set-up, starting with a higher relative abundance of CH_4 results in higher tholin production yields and therefore thicker samples, which results in higher-quality analytical measurements. Finally, the purpose of adding 0.5% of C_2H_2 in half of the gas mixtures is to study chemical processes which occur at later stages of the chemistry that leads to the tholin formation in COSmIC, as the residence time of the gases in the chamber in the plasma discharge is short and truncates the chemistry (see below). The addition of C_2H_2 also allowed us to compare our results with previous experiments (Sciamma-O'Brien et al., 2014, 2017).

The gas mixtures were introduced into the COSmIC chamber, exposed to a pulsed plasma discharge generated with a −800-V high voltage used as the energy source to induce the chemistry, and deposited for 1–2 h (to ensure very little material was deposited; see Section 3.5) onto silicon nitride (Si_3N_4) substrates placed 5 cm away from the slit, i.e., at the same distance as the substrates shown in Fig. 1(b). The voltage chosen for these experiments, which is higher than the voltage used in previous experiments (Sciamma-O'Brien et al., 2014, 2017), resulted in a higher production of samples in a shorter amount of time. We expect the chemistry to be slightly different with −800 V than with −700 V, however, this does not impact the results of this study whose main goal is to compare 4 tholin samples produced under the same experimental conditions at −800 V. The solid deposits were then collected in a glove box connected to the vacuum chamber and stored under an argon atmosphere in sealed containers with desiccant until further analysis. The four tholin samples were therefore exposed to air only at the time of their characterization by XANES spectroscopy, as described below.

2.2. *XANES analysis of tholins*

X-ray absorption near-edge structure (XANES) spectroscopy is a synchrotron-based soft-X-ray micro-analytical technique that can be used to assess both the functional groups present in a sample and the relative elemental abundances between the elements studied. XANES spectroscopy at the carbon (C), nitrogen (N), and oxygen (O) 1s edges has been extensively used to study organic compounds in extraterrestrial samples such as meteorites, interplanetary dust particles (IDPs), and cometary grains returned by the NASA Stardust mission (Bajt et al., 1996; Keller et al., 2004; Sandford et al., 2006; Cody et al., 2008; Matrajt et al., 2008; Wirick et al., 2009; De Gregorio et al., 2013). XANES spectroscopy has also been used to study laboratory refractory residues produced from the simultaneous deposition and UV irradiation of astrophysical ice mixture analogs (H_2O, CH_3OH, CO, NH_3, etc.) at low temperature (20 K) (Nuevo et al., 2011), as well as laboratory refractory organic materials produced from the UV irradiation or 1.2-keV electron bombardment of N_2:CH_4:CO (100:1:1) ice mixtures at 15 K, analog to the surface materials on Pluto and other trans-Neptunian objects (TNOs) and hereafter referred to as Pluto/TNO tholins (Materese et al., 2014, 2015). In addition, prior to this study, XANES spectroscopy analysis of Titan tholins has been reported only once for a sample produced from a N_2:CH_4 (95:5) gas mixture in another experimental set-up that uses a radiofrequency (RF) plasma to induce chemistry (Kuga et al., 2014). XANES spectroscopy is thus well suited for the study of the Titan tholins produced with COSmIC/THS, as the tholin production rate is extremely low in our experiments, which makes it difficult to use more commonly used combustion methods to obtain information on their elemental composition.

The tholin samples produced in this study were deposited on silicon nitride (Si_3N_4) windows, which are suitable for XANES measurements. XANES measurements were conducted using the scanning transmission X-ray microscope (STXM) mounted on beamline 5.3.2.2 of the Advanced Light Source of the Lawrence Berkeley Laboratory. The STXM provides photons in the 250–700 eV range with a 10^7 photons s^{-1} flux (Kilcoyne et al., 2003). XANES spectra of the tholin samples were acquired in the 275–580 eV energy range in order to span the carbon (275–340 eV), nitrogen (385–440 eV), and oxygen (520–580 eV) 1s X-ray absorption edges, with an energy step size of 0.1 eV in the fine structure regions, and 1–2 eV in the pre- and post-edge regions (Cody et al., 2008; Nuevo et al., 2011). All STXM data were reduced and analyzed using the aXis 2000 software.[1]

The C-, N-, and O-XANES spectra provided information on the functional groups present in the tholin samples. In addition, the XANES spectra measured over the full 275–580 eV energy range were used to derive the relative elemental abundances between C, N, and O for each tholin sample. This was done by computationally fitting the full-range XANES spectra of all tholins spanning the C, N, and O 1s edges with the atomic mass absorption coefficients (Henke et al., 1993) to estimate the overall increase in absorption above the ionization C, N, and O edges relative to the absorption below these ionization edges. This is possible for low-*Z* elements, for which absorption in the soft-X-ray range is dominated by photo-ionization cross sections, and for which atomic scattering is very weak (Stöhr, 1992). These abundances were then used to determine the C/N and C/O ratios for each tholin sample, using the approach described in Cody et al. (2008) and Nuevo et al. (2011).

3. Results and discussion

3.1. *Carbon XANES spectra*

The normalized C-XANES spectra of all four tholins (Fig. 2) show the presence of a variety of functional groups. Table 1 lists the main bands present in all tholin samples. They are associated with aromatic carbon (band C1 at ~285.2 eV), imines (C=N; band C2 at ~285.9 eV), and nitriles (C≡N; band C3 at ~286.8 eV) (see Fig. 2 and Table 1). The relative proportions between these bands and the rest of the spectra vary significantly from one sample to another, although they appear to be more intense (relative to other bands) for tholins produced from the two gas mixtures containing acetylene (C_2H_2) (Fig. 2). Higher formation yields for aromatic compounds when acetylene is present are consistent with (i) previous mass spectrometry experiments conducted on COSmIC which showed that the addition of C_2H_2 in gas mixtures in which Ar or N_2 is the main component leads to the production of benzene in the gas phase (Contreras and Salama, 2013; Sciamma-O'Brien et al., 2014), and (ii) the fact that C_2H_2 is a known precursor of benzene in astrophysical environments (Frenklach and Feigelson, 1989; Cherchneff et al., 1992; Jäger et al., 2009; Zhao et al., 2016). Two other bands, assigned to amide groups and/or benzene (band C4 at 287.8–288.3 eV) and amorphous carbon, alcohols, and/or urea groups (band C5 at 288.9–289.7 eV), are also present in all tholins with varying intensities. Note that if a band is assigned to more than one functional group or structure, it may indicate the presence of either only one of these groups or several of them. In the case of the band C4, the presence of amide groups is supported by the band O3 in the O-XANES spectra (see Fig. S1 and Table S3 in the Supplementary Material). However, the contribution of benzene to this band, and thus its presence in the tholins, should not be ruled out, in particular in the tholins produced from the gas mixtures that contained acetylene, because acetylene is a well-known precursor to benzene (Frenklach and Feigelson, 1989; Cherchneff et al., 1992; Jäger et al., 2009; Zhao et al., 2016). Similarly, although the presence of alcohols and/or urea groups (band C5) is supported by the band O4 (alcohols) and a band at 532.1–532.2 eV (carboxyls) in Fig. S1 and Table S3, the presence of amorphous carbon should not be ruled out. The presence of O-bearing groups is believed to be mainly due to oxidation of the tholin samples when exposed to air during the transfer to the STXM vacuum chamber to conduct XANES measurements, rather than from plasma-induced chemistry in the COSmIC/THS experiments, as discussed in more detail in Section 3.5.

The C-XANES spectra of all four tholin samples also show the presence of multiple minor bands assigned to a wide variety of chemical functions (Table S1, Supplementary Material). Most of these assignments are tentative, as the intensities of most of these bands are small. Among these, bands at ~283, 284.6, ~286, and ~290.5 eV are associated with the presence of amorphous carbon (Table S1), which is mixed with aromatic carbon structures (band C1, 285.0–285.3 eV; Table 1) and aliphatic carbon chains (bands at ~287–288.5 eV; Table S1). The bands assigned to aliphatic carbon chains appear to be the strongest in the spectrum of the tholin sample produced from the N_2:CH_4 (90:10) mixture. A complete list of the bands observed in all four tholins is shown in Table S1. Other minor bands consistent with the presence of different types of aromatic materials are also observed in all tholins, including nitrogen-bearing heterocyclic

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[1] aXis 2000 is written in Interactive Data Language (IDL) and available for free for non-commercial use from http://unicorn.mcmaster.ca/aXis2000.html.

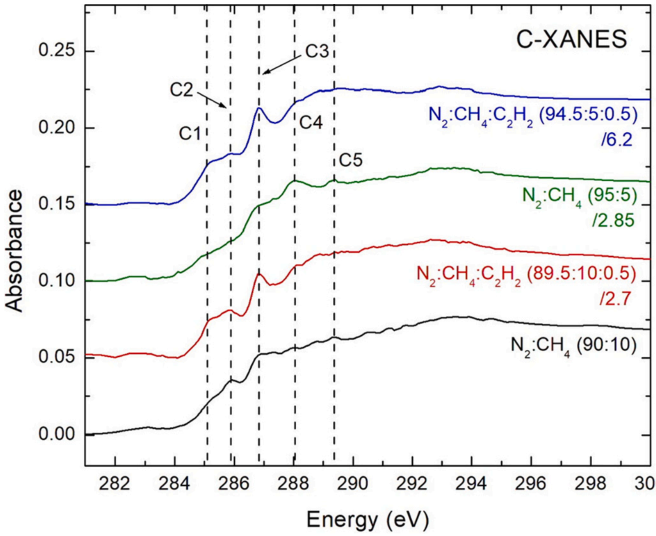

Fig. 2. XANES spectra at the carbon 1s edge of the four tholin samples produced in the present study. The intensities of the spectra are normalized to the C-edge peak intensity of the N_2:CH_4 (90:10) spectrum. Normalization factors are provided below each gas mixture composition on the plot. The main bands (C1–C5) are highlighted with dashed lines and their assignments are given in Table 1. Minor bands are listed in Table S1 (Supplementary Material). Absorbances of the spectra are offset for clarity.

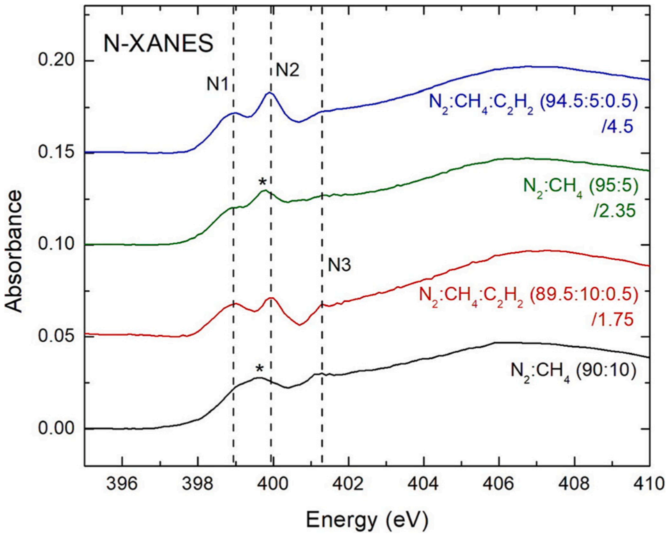

Fig. 3. XANES spectra at the nitrogen 1s edge of the four tholin samples produced in the present study. The intensities of the spectra are normalized to the N-edge peak intensity of the N_2:CH_4 (90:10) spectrum. Normalization factors are provided below each gas mixture composition on the plot. The main bands (N1–N3) are highlighted with dashed lines and their assignments are given in Table 1. Minor bands are listed in Table S2 (Supplementary Material). The bands marked with an asterisk correspond to the band N2 that is redshifted in energy and referred to as band N2* (Table 1, Section 3.2). Absorbances of the spectra are offset for clarity.

compounds, but are stronger for tholins produced from mixtures containing C_2H_2; these bands are consistent with the presence of C- and N-bearing compounds similar to graphite (~285.2 and ~291.5 eV), pyridine (C_5H_5N; ~286.9 and ~290.6 eV), and fullerene (C_{60}; ~290.6 eV) (Table S1). However, it is difficult to estimate the relative intensities between aromatic hydrocarbons and heterocyclic aromatic hydrocarbons because most of these bands are weak and overlap with each other as well as with other bands.

The C-XANES spectra of both our N_2:CH_4 tholins (90:10 and 95:5) are consistent with the only other XANES study of a Titan tholin produced from a N_2:CH_4 (95:5) mixture in an RF plasma experimental setup reported by Kuga et al. (2014). The two most intense bands observed in Kuga et al. (2014)'s C-XANES spectrum at 286.8 and 288.1 eV, assigned to nitriles/ketones and aliphatic carbon/amides, respectively, correspond to the bands C3 and C4 observed in our C-XANES spectra (Fig. 2, Table 1). The C-XANES spectra of our four tholin samples also share strong similarities with those obtained in a XANES study of two laboratory-generated Pluto/TNO tholins produced from the UV photo-irradiation and 1.2-keV electron bombardment of N_2:CH_4:CO (100:1:1) ice mixtures (Materese et al., 2014, 2015). In particular, the C-XANES spectra of our four tholins and these two Pluto/TNO tholins show the presence of aromatic carbon (285.0–285.3 eV) and nitriles (399.3–400.0 eV).

Table 1
Assignments of the main bands observed at the carbon (C1–C5, Fig. 2) and nitrogen (N1–N3, Fig. 3) 1s edge XANES spectra of all four tholins. A more complete list of possible assignments of all the bands (including minor bands) in these C- and N-XANES spectra are listed in Tables S1 and S2 (Supplementary Material), respectively. The band N2* corresponds to the band N2 that is redshifted in tholins produced from gas mixtures that did not contain acetylene (Fig. 3). C and N atoms involved in their respective XANES bands are marked in bold.

	Band	Energy (eV)	Assignment	Transition	References[†]
Carbon edge	C1	285.0–285.3	Aromatic **C**=C	1s → π*	1,2,3
	C2	285.7–286.0	Imine **C**=N	1s → π*	4,5
	C3	286.8–287.0	Nitrile **C**≡N	1s → π*	2,4,6,7,8
	C4	287.8–288.3	Amide O=**C**–NH$_x$	1s → π*	2,9
	C4	287.9–288.2	Benzene [Ar]**C**	1s → π*	10
	C5	288.9–289.2	Amorphous C (*sp*^{3})	1s → 3p/σ*	10
	C5	288.9–289.4	Alcohol **C**H$_x$–OR	1s → 3p/σ*	11,12,13
	C5	288.9–289.7	Urea group (NH$_x$)$_2$**C**=O	1s → π*	2
Nitrogen edge	N1	398.2–399.1	Imine C=**N**	1s → π*	2,7,14
	N2*	399.3–399.8	Nitrile (aliphatic) C≡**N**	1s → π*	2,5,14,15,16
	N2	399.8–400.0	Nitrile (aromatic) C≡**N**	1s → π*	17
	N3	401.0–401.3	Amide O=C–**N**H$_x$	1s → π*	2,3,14,18
	N3	401.0–401.4	Heterocyclic N	1s → π*	15
	N3	401.1–401.4	Amine C–**N**H$_x$	1s → 3p/σ*	3

[†] References: (1) Stöhr (1992); (2) Cody et al. (2008); (3) Cody et al. (2011); (4) Dhez et al. (2003); (5) Shard et al. (2004); (6) Kikuma et al. (1998); (7) Apen et al. (1993); (8) Zhou et al. (2009); (9) Urquhart and Ade (2002); (10) Díaz et al. (2001); (11) Ishii and Hitchcock (1988); (12) Sham et al. (1989); (13) Lehmann et al. (2005); (14) Leinweber et al. (2007); (15) Pels et al. (1995); (16) Ray et al. (2005); (17) Zhu et al. (1997); (18) Gordon et al. (2003).

3.2. Nitrogen XANES spectra

The normalized N-XANES spectra for all four of our tholin samples (Fig. 3) are consistent with their C-XANES spectra (Fig. 2, Section 3.1). Table 1 lists the main bands observed in all tholin samples. They are associated with imines (band N1 at 398.9–399.2 eV in Fig. 3) and nitriles (band N2 at 399.8–400.0 eV), in particular for the tholins produced from mixtures containing C_2H_2. In the spectra of tholins produced from mixtures that did not contain acetylene, the band N2 is slightly redshifted (band N2* at 399.3–399.8 eV), indicating that the nitrile groups are mostly linked to aliphatic carbon chains (Pels et al., 1995; Shard et al., 2004; Ray et al., 2005; Leinweber et al., 2007; Cody et al., 2008), as opposed to nitrile groups linked to aromatic hydrocarbons (band N2) (Zhu et al., 1997). Another band (N3 at ~401.3 eV) that is observed in all spectra can be assigned to amino groups (Cody et al., 2011), although the position of this band is also consistent with the presence of amide groups (O=C–NH$_x$) and mirrors the presence of the bands C4 in the C-XANES spectra (Fig. 2 and Table 1) and O3 in the O-XANES spectra (Fig. S1 and Table S3, Supplementary Material).

N-XANES spectra also contain several minor bands that are tentatively associated with a wide variety of functional groups or compounds

(Table S2, Supplementary Material), including pyridine, pyrrole, different types of nitrogen heterocycles, nitroso groups, nitro groups, and oxidized variants of pyridine (pyridone and pyridine *N*-oxide). However, the assignments of these O-bearing species could not be confirmed by the presence of mirror bands in the O-XANES spectra (Table S3, Supplementary Material). Finally, multiple weak bands at ~400.5, ~401.3, and ~407.0 eV are consistent with the presence of nitrogen atoms inserted in graphene structures, supporting the bands associated with graphene-like structures in the C-XANES spectra (Section 3.1, Table S1).

As was the case for the C-XANES spectra, the N-XANES spectra of the four tholin samples studied here share similarities with the only other XANES spectrum of another Titan tholin sample produced from a N_2:CH_4 (95:5) gas mixture in a different experimental set-up (Kuga et al., 2014). In particular, the spectrum of our tholin sample produced from the N_2:CH_4 (95:5) gas mixture is very similar to that of Kuga et al. (2014), in which the two main bands observed at 398.9 and 399.7 eV, assigned to imines and nitriles, respectively, are comparable to the bands N1 and N2/N2* in our N-XANES spectra. The Pluto/TNO tholins reported by Materese et al. (2014, 2015) also share similarities with our tholin samples, with bands at 399.9 and 401.0 eV associated with nitriles and amides, respectively, comparable to the bands N2/N2* and N3 observed in our N-XANES spectra. In addition, although not explicitly reported in Materese et al. (2014, 2015), a shoulder visible in the N-XANES spectra of the Pluto/TNO tholins around 398–399 eV is consistent with the presence of imines, i.e., comparable to band N1 in our N-XANES spectra.

3.3. C/N ratios and nitrogen content

The elemental C/N abundance ratios derived from fitting the full-range XANES spectra (Fig. 4) with atomic mass absorption coefficients (Henke et al., 1993; Section 2.2) for the four tholins studied here are summarized in Table 2. The error bars on these ratios are due to the method used to fit the XANES spectra to the atomic mass absorption coefficients (Cody et al., 2008; Nuevo et al., 2011). C/N ratios were found to be low, in the 0.9–2.4 range. These values are consistent with the C/N ratios obtained using combustion and pyrolysis techniques for other tholins produced in experimental set-ups which use energy sources that can dissociate N_2 (i.e., cold plasma or extreme UV radiation sources) (Cable et al., 2012). Note that an increase (respectively, decrease) in the C/N ratio can be due to an increase (respectively, decrease) in the relative abundance of C and/or a decrease (respectively, increase) in the relative abundance of N.

Our tholins produced from gas mixtures without acetylene display lower C/N ratios (0.9–1.3) than those produced from mixtures with acetylene (2.2–2.4). This increase by a factor of 2 in the C/N ratios of the tholin samples produced from the gas mixtures with C_2H_2 is correlated with an increase in the abundance of aromatic carbon, imines, and nitriles observed in these samples (Fig. 2, Section 3.1). These observations indicate that the addition of acetylene by as small a mixing ratio as 0.5% in the initial gas mixture results in a significant increase in the formation of chemical groups that consist of double and triple covalent bonds (C=C, C=N, and C≡N). In addition, the nitrile band (band N2 in Fig. 3 and Table 1) of the tholin samples produced from mixtures that contained acetylene tends to be shifted to higher energies, implying a larger proportion of nitrile groups attached to aromatic structures, as opposed to aliphatic structures (band N2*) (Section 3.2).

A plausible explanation for these observations resides in the design of the COSmIC/THS experimental set-up, which only allows for the first steps of the chemistry to occur, due to the short residence time (~3.5 μs) of the gas in the plasma discharge. This truncated chemistry was demonstrated by a mass spectrometry study of the plasma-generated gas-phase products (Sciamma-O'Brien et al., 2014), and subsequently confirmed by a modeling study of the gas phase (Raymond et al., 2018). These studies indicated that, in the COSmIC/THS experiment, plasmas generated in gas mixtures containing heavier molecular precursors result in the production of heavier molecular products. The presence of heavier precursors in the initial gas mixtures allows to go further into the chemistry and highlights the pathways associated with that precursor, leading to the formation of larger molecules within the short residence time of the gas in the plasma cavity. However, the use of heavier precursors can also lead to a chemistry favoring specific chemical pathways that involve these initial precursors and/or dominant products formed from these precursors.

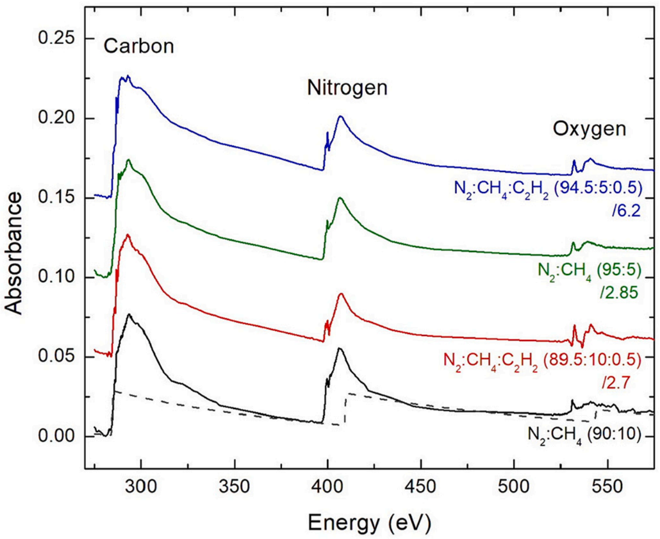

Fig. 4. Full-range XANES spectra spanning the C, N, and O 1s edges of the four tholin samples produced in the present study. The intensities of the spectra are normalized to the C-edge peak intensity of the N_2:CH_4 (90:10) spectrum. Normalization factors are provided below each gas mixture composition on the plot. These spectra were used to determine the C/N and C/O ratios of each sample, after fitting the spectra with atomic mass absorption coefficients (see Sections 3.3 and 3.5, respectively). An example of such computational fit is shown for the spectrum of the tholin produced from the N_2:CH_4 (90:10) gas mixture (dashed curve). Detailed XANES spectra at the C and N 1s edges are shown in Figs. 2 and 3, respectively, and the assignments of the bands at the C and N edges are given in Table 1. Detailed XANES oxygen 1s edge spectra are shown in Fig. S1 and the assignments of the bands are given in Tables S1 and S2 (Supplementary Material). Absorbances of the spectra are offset for clarity.

Table 2
Elemental C/N ratios determined from fitting the full-range XANES spectra of all tholins spanning the C, N, and O 1s edges (Fig. 4) with the atomic mass absorption coefficients (Henke et al., 1993, see Sections 2.2 and 3.3 for details). Error bars are due to the fitting method used (Cody et al., 2008; Nuevo et al., 2011).

Initial gas mixture	C/N Ratio
N_2:CH_4 (90:10)	0.9 ± 0.3
N_2:CH_4:C_2H_2 (89.5:10:0.5)	2.2 ± 0.4
N_2:CH_4 (95:5)	1.3 ± 0.2
N_2:CH_4:C_2H_2 (94.5:5:0.5)	2.4 ± 0.4

In addition, in an IR spectroscopy study of the solid-phase products formed in the COSmIC/THS set-up (Sciamma-O'Brien et al., 2017), it was observed that both the nitrogen chemistry and the incorporation of N atoms into the solid phase vary depending on the composition of the initial gas mixture. In particular, when acetylene was present in the mixture, the chemistry appeared to favor the formation of aromatic hydrocarbons, in which fewer N atoms were incorporated into the tholins. The IR bands associated with N-bearing functional groups showed that N atoms were added to the periphery of the molecules rather than deeper inside the molecular structure, which is consistent with the findings of the present study. A possible explanation for the higher C/N ratios reported here for tholins produced from mixtures containing acetylene as well as from the IR spectroscopy results reported in Sciamma-O'Brien et al. (2017) is that the high reactivity of C_2H radicals produced from the dissociation of C_2H_2 (Herbst and Woon, 1997; Agúndez and Wakelam, 2013) triggers a chemistry in which the formation of hydrocarbons is favored over that of N-bearing molecules during the short 3.5-μs residence time of the gas in the plasma cavity, which results in more aromatic hydrocarbons being formed and less nitrogen being incorporated in a bottom-up-type chemistry starting with smaller molecules.

When comparing the C/N ratios of the tholin samples produced from N_2:CH_4 and N_2:CH_4:C_2H_2 gas mixtures with different concentrations of CH_4, we also observe that an increase in the concentration of CH_4 (from 5% to 10%) results in a slight decrease in the C/N ratio for both the samples produced from N_2:CH_4 mixtures (from 1.3 to 0.9) and those produced from N_2:CH_4:C_2H_2 mixtures (from 2.4 to 2.2). Although this observation suggests that more N atoms may be incorporated into the tholins when the initial gas mixture contains more CH_4, in particular because this change in C/N ratio is observed for both N_2:CH_4 and N_2:CH_4:C_2H_2 mixtures, note that the uncertainties associated with the C/N ratio values (Table 2) are large enough for the C/N ratios to be considered as constant for a given gas composition (N_2:CH_4 or N_2:CH_4:C_2H_2) when the CH_4 concentration increases.

Our XANES results, in which we observed lower C/N ratios and smaller amounts of nitriles in tholins produced from mixtures not containing C_2H_2, are also consistent with a previous IR study of our COSmIC/THS tholins (Sciamma-O'Brien et al., 2017). The lower level of incorporation of nitrogen in the tholins formed from N_2:CH_4:C_2H_2 mixtures is also consistent with the findings of a recent study of the surface energy of tholins produced in the COSmIC set-up from N_2:CH_4 (95:5) and N_2:CH_4:C_2H_2 (94.5:5:0.5) gas mixtures (Li et al., 2021). The effects of varying the concentration of CH_4 and/or adding acetylene as a precursor in the initial gas mixtures therefore reveal significant differences in how nitrogen is incorporated into the solid phase of our tholin samples.

3.4. Comparison with C/N ratios from the literature

From a general standpoint, it is difficult to conduct a rigorous comparison of the C/N ratios determined for the tholins of our study with other Titan tholins produced in previous, independent studies reported in the literature (e.g., McDonald et al., 1994; Coll et al., 1995, 1997, 1999, 2001; McKay, 1996; Sarker et al., 2003; Tran et al., 2003, 2008; Imanaka et al., 2004; Curtis et al., 2005; Ferris et al., 2005; Somogyi et al., 2005; Bernard et al., 2006; Szopa et al., 2006; Neish et al., 2008; Quirico et al., 2008; Sekine et al., 2008; Carrasco et al., 2009, 2016; Imanaka and Smith, 2010; Sciamma-O'Brien et al., 2010; Cable et al., 2012), as these tholins were produced using a wide range of experimental set-ups with many varying parameters (gas mixture composition, energy source, pressure, temperature, etc.) that could all have an impact on the final measured C/N ratios.

To the best of our knowledge, before the study presented here with the COSmIC experimental set-up, only two other experimental set-ups were used to conduct systematic C/N ratio studies of tholins produced with different concentrations of methane. McDonald et al. (1994) used a continuous flow plasma experiment at room temperature with a pressure of 1.5 mbar to produce tholins from N_2:CH_4 gas mixtures with 0.1% and 10% of CH_4 and did observe a decrease in the C/N ratio when increasing the CH_4 mixing ratio (C/N ratios of 1.49 and 0.75 for CH_4 concentrations of 0.1% and 10%, respectively), which is in agreement with the trend we observe in the COSmIC study presented here (C/N ratios of 1.3 and 0.9 for CH_4 concentrations of 5% and 10%, respectively). The opposite trend was reported for tholins produced in another experimental set-up (PAMPRE) at room temperature and 1–2 mbar pressure in a continuous flow plasma experiment (Quirico et al., 2008; Sciamma-O'Brien et al., 2010; Carrasco et al., 2016), where a higher C/N ratio was observed for tholins produced with higher concentration of CH_4, with C/N ratios of 1.67 and 2.5 for CH_4 concentrations of 5% and 10%, respectively (Carrasco et al., 2016). These opposite trends in published data show the complexity of comparing the results obtained from different experiments.

For instance, if we look at the only other experimental set-up (PAMPRE) that was used to conduct systematic studies in which tholins were produced from concentrations of CH_4 of 5% and 10% and their C/N ratios were determined (Sciamma-O'Brien et al., 2010; Carrasco et al., 2016), an increase by a factor of 1.5 in the C/N ratio of the PAMPRE tholins was observed when increasing the concentration of CH_4 in the initial N_2:CH_4 gas mixture from 5% to 10%. This trend is the opposite of what we observe in the COSmIC tholins, where the C/N ratio decreases by a factor of 1.4 when the CH_4 concentration increases from 5% to 10% (Table 2, Section 3.3). In the PAMPRE experiment, however, a continuous plasma is used, and the set-up is designed so that the aerosols remain in levitation and grow in the plasma discharge for a long time (~100 s; Alcouffe et al., 2010). In contrast, in the COSmIC experiment, a pulsed plasma is used in the stream of an accelerated gas expansion, and the residence time of the gas in the plasma cavity is ~3.5 μs, which means that the residence time of the aerosols, which are carried by the accelerated pulsed gas expansion, is shorter than 3.5 μs (Sciamma-O'Brien et al., 2014). The very short residence time in COSmIC results in truncated chemistry and aerosol growth (Sciamma-O'Brien et al., 2014, 2017; Raymond et al., 2018), while the longer residence time in PAMPRE allows the chemistry to progress much farther. This difference could change the way nitrogen is incorporated into the solid phase and explain the opposite trends observed in the PAMPRE and COSmIC experiments.

Another difference between the PAMPRE and COSmIC experimental set-ups that could explain the opposite trends observed for the C/N ratios is the operating gas temperature in the reaction chamber (room temperature for PAMPRE vs. 150 K for COSmIC), which could result in different chemical pathways, changing the nitrogen incorporation into the solid phase. The significant effect of the operating gas temperature on the tholin C/N ratios has been demonstrated by Coll et al. (1999). In their experiments, Coll et al. produced tholins via plasma chemistry at room temperature and 100–150 K from N_2:CH_4 (98:2) gas mixtures at low pressure (1.5 mbar). The C/N ratios determined for the resulting tholins were 1.73 at room temperature and 2.82–2.83 at 100–150 K. This study thus highlighted an important effect of the gas temperature on the chemistry and in particular the nitrogen incorporation, and may explain why the evolution of the C/N ratio as a function of the concentration of CH_4 in the initial mixture in our experiments is different from what is observed in the PAMPRE experiments.

Other factors like the gas pressure and the energy flux inducing the chemistry most likely also contribute to the differences observed in the chemistry and the nitrogen incorporation into the solid phase between the PAMPRE and COSmIC experimental set-ups. This demonstrate how difficult comparative analyses can be between different experimental set-ups. Only systematic and purposeful comparative studies where specific parameters are varied to observe their effects on the properties of the tholins (optical constants, physical and bulk properties, composition) will shed some light on the differences observed between different experimental set-ups. All three experimental set-ups that have conducted C/N ratio studies of tholins produced in different gas mixtures have however demonstrated that the initial composition has an effect on the way nitrogen is incorporated into the solid phase, which is a piece of the puzzle towards unveiling the complexity of Titan's chemistry.

3.5. Oxygen-bearing compounds and C/O ratios

Although oxygen was not present in any of the initial starting gas mixtures, its contribution to the full-range XANES spectra is non negligible. Indeed, Fig. 4 shows that the intensity of the O edge is 5–8 and 2–4 times smaller than the intensities for the C and N edges, respectively. This means that a measurable amount of oxygen was incorporated into the tholins during the few minutes they were transferred onto the sample holders to be placed into the STXM device for XANES analysis. Oxidation of the tholin samples is supported by the presence of multiple oxygen-bearing functional groups in the C-XANES and N-XANES spectra of all tholins, in particular amides and alcohols (Table 1), as well as other types of carbonyls (Tables S1 and S3). The corresponding normalized O-XANES spectra of the four tholins produced in this study are shown in Fig. S1, and the complete list of the band assignments is given in Table S3, both in the Supplementary Material.

The presence of O-bearing groups in all our tholin samples may be explained by the structure of the tholin samples produced in these experiments. Because materials analyzed with the STXM instrument need to be thin enough for the X-rays to penetrate through the full thickness of the samples, the tholins studied here were produced from experiments that lasted 1–2 h, resulting in substrates covered with scattered individual grains, 100–500 nm in diameter (depending on the initial mixture), separated from each other on the substrate. In contrast, during longer experiments, in which the tholins are typically recovered after 10–40 h of sample production, the grains jet-deposited on the substrate stack on top of each other, forming a more homogeneous layer of material (Sciamma-O'Brien et al., 2017). Consequently, oxidation will affect a larger fraction of the samples produced from shorter experiments, as the ratio between the surface exposed to oxidation and the volume of material is much higher for samples consisting of individual grains (i.e., shorter experiments) than for samples consisting of a homogeneous deposit (i.e., longer experiments). In Carrasco et al. (2016), the layer of oxidation of a Titan tholin sample produced from an oxygen-free N_2:CH_4 (90:10) initial mixture was measured to be about 20 nm thick. Considering spherical grains with a diameter of 500 nm for our tholin samples produced from gas mixtures containing C_2H_2 (Sciamma-O'Brien et al., 2017), a 20-nm-thick oxidation layer would correspond to an oxidation level of about 22% of the total volume. However, the tholin sample produced by Carrasco et al. (2016) was not kept under inert atmosphere and was therefore exposed to air for a long period of time before characterization. Since our tholin samples were kept under an argon atmosphere and exposed to air for only a few minutes before being analyzed, the thickness of the oxidation layer is expected to be smaller than 20 nm. Nonetheless, because the tholin samples produced in our XANES study have a large surface-to-volume ratio, their XANES spectra are more susceptible to higher relative levels of oxidation, as confirmed by the high abundances of O-bearing groups (Fig. S1 and Table S3, Supplementary Material).

Kuga et al. (2014) also reported the presence of O-bearing functional groups in the C- and N-XANES spectra of their Titan tholin sample produced from an oxygen-free N_2:CH_4 (95:5) initial mixture. They observed bands associated with amides, alcohols, and ethers, which are also present in all our tholin samples (Tables 1, S1, and S2). Previous tholin studies showed that unsaturated chemical groups in the molecular structure of tholins produced by cold plasmas are dominated by nitrogen-bearing moieties (i.e., imines, nitriles), which may explain why tholins are easily prone to hydrolysis and therefore oxidation (Cable et al., 2012).

Finally, the elemental C/O abundance ratios (and their associated error bars) derived for the four tholins studied here are summarized in Table S4 (Supplementary Material). These ratios were determined to range from 1.9 to 3.3, with higher C/O ratios for tholins produced from initial mixtures containing acetylene. A previous scanning electron microscopy (SEM) study of COSmIC/THS tholin samples (Sciamma-O'Brien et al., 2017) demonstrated that tholins produced from N_2:CH_4:C_2H_2 gas mixtures consist of grains with much larger diameter than tholins produced from simpler N_2:CH_4 mixtures (500 nm vs. 100 nm). This implies that the surface-to-volume ratio of the tholin samples produced from C_2H_2-containing mixtures is much smaller than for tholins produced in mixtures without C_2H_2, which results in a lower oxidation level of the samples when exposed to air. The observation of higher C/O ratios for the tholins produced in C_2H_2-containing mixtures are therefore consistent with the hypothesis that oxidation most probably occurred when the tholins were exposed to air during their transfer to the sample holder to be analyzed with the STXM instrument rather than during the experiments inside the COSmIC/THS chamber.

3.6. *Applications to Titan's atmosphere*

The XANES study at the C and N edges of the tholin samples produced in our COSmIC/THS experimental set-up from four different initial gas mixtures, namely, N_2:CH_4 (90:10 and 95:5) and N_2:CH_4:C_2H_2 (89.5:10:0.5 and 94.5:5:0.5), showed that the relative abundances between the C- and N-bearing products that are formed vary with both the presence or absence of C_2H_2 and possibly the relative proportion of CH_4 in the initial gas mixtures. XANES spectra of these tholins also showed that mixtures containing C_2H_2 favored the formation of aromatic compounds and larger relative amounts of imines and nitriles compared to mixtures without C_2H_2.

These important results can be used to infer some connections with what can be expected for the production mechanisms of the aerosols that are responsible for the haze layers in Titan's atmosphere. Indeed, the variations observed for the composition and C/N ratios of our four tholin samples can be interpreted as potential indicators of variations in the composition of Titan's haze, as predicted by photochemical models (Wilson and Atreya, 2003; Lavvas et al., 2008a, 2008b). Our experimental results confirm that the nitrogen content of Titan's aerosols is expected to vary over seasonal and astronomical timescales (Lunine and Atreya, 2008; Roe, 2012).

The nitrogen content of Titan's aerosols is also expected to vary as a function of the altitude and latitude at which the aerosols are formed, particularly during seasonal changes that affect the atmospheric circulation and result in a molecular enrichment at the poles. For example, molecules such as C_2H_2, C_2H_4, C_2H_6, C_6H_6, HC_3N, and HCN were observed in higher concentrations at the south pole after the northern spring equinox, where they are expected to have an impact on the composition of the aerosols formed at these latitudes (e.g., Teanby et al., 2012; Vinatier et al., 2015; Coustenis et al., 2016; Mathé et al., 2020). Our experimental results demonstrate that a change in the atmospheric composition due to these seasonal and local enhancements would influence the chemistry and the resulting aerosol production mechanisms. The low C/N ratios measured for all our tholin samples are also consistent with the hypothesis that Titan's aerosols act as a sink for N atoms in the atmosphere, as supported by the data collected by *Huygens*' Aerosol Collector Pyrolyser (Israël et al., 2005).

4. Conclusions

We produced Titan tholins in the COSmIC/THS experimental set-up using a plasma discharge in the stream of a jet-cooled expansion for four different initial gas mixtures: N_2:CH_4 (90:10 and 95:5) and N_2:CH_4:C_2H_2 (89.5:10:0.5 and 94.5:5:0.5). The tholin samples were collected under inert atmosphere after 1–2 h of deposition and were analyzed with XANES spectroscopy at the C, N, and O edges. The absorption bands identified in the XANES spectra of these tholin samples indicate the presence of various chemical structures and groups, including aromatic carbon, imines, and nitriles. The relative abundances between these bands vary with (i) the presence or absence of C_2H_2, and (ii) possibly the concentration of CH_4 in the initial mixtures. COSmIC/THS experiments conducted with initial mixtures in which C_2H_2 was added resulted in the formation of tholins that contain more aromatic compounds and larger relative amounts of imines and nitriles compared with tholins produced from mixtures that did not contain C_2H_2. XANES spectra of all tholins also show the presence of O-bearing species that resulted from the oxidation of the tholins when exposed to air. Furthermore, XANES spectroscopy was used to determine the elemental C, N, and O composition of our four tholin samples, and to estimate their C/N and C/O ratios. C/N ratios were all found to be low (< 2.5), in agreement with previous, independent studies of tholins produced with energy sources that can dissociate N_2. C/N ratios were found to be slightly lower when the concentration of CH_4 in the gas mixture was higher. Finally, the C/N ratios of tholins produced from gas mixtures that contained C_2H_2 were found to be twice as large as of those produced from mixtures that did not contain C_2H_2, demonstrating the impact of the composition of the initial gas on the composition of the resulting solid-phase particles, in particular the nitrogen incorporation.

The differences in chemical (aromatic vs. aliphatic compounds, nitriles, etc.) and elemental (C/N ratios) compositions, observed for our COSmIC/THS tholins produced from gas mixtures with different concentrations of CH_4 and in the absence/presence of C_2H_2, highlight differences in how nitrogen is incorporated into the solid phase: when C_2H_2 is absent from the initial mixture, nitrogen is incorporated deeper in the molecular structure and nitrile groups are preferably attached to aliphatic structures, while when C_2H_2 is present, nitrogen is added to the periphery of aromatic molecules, for example in the form of nitrile groups.

Our experimental results can also guide the interpretation of observations of Titan's atmosphere and the development of models. Indeed, the differences in chemical and elemental compositions of our tholins illustrate how a change in composition at the location where aerosols are formed in Titan's atmosphere may lead to variations in the nitrogen content and composition of Titan's aerosols. This variability depends on several parameters which need to be taken into account in models, such as the location (altitude, latitude), the season, and the astronomical timescales, as they can affect the atmospheric circulation, the concentration of specific molecules in different parts of the atmosphere, and therefore the chemistry and product formation.

Declaration of Competing Interest

None.

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Appendix A. Supplementary material

Supplementary material and data to this article can be found online at https://doi.org/10.1016/j.icarus.2021.114841.

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