



## Experimental laboratory simulation of Titan's atmosphere: aerosols and gas phase

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### Abstract

The discovery that Titan, the largest satellite of Saturn, has an atmosphere and that methane is a significant constituent of it, was the starting point for a systematic study of Titan's atmospheric organic chemistry. Since then, the results from numerous ground-based observations and two flybys of Titan, by Voyager I and II, have led to experimental laboratory simulation studies and photochemical and physical modeling. All these works have provided a more detailed picture of Titan. We report here a continuation of such a study performing an experimental laboratory simulation of Titan's atmospheric chemistry, and considering the two physical phases involved: gases and aerosols. Concerning the gaseous phase, we report the first detection of C<sub>4</sub>N<sub>2</sub> and we propose possible atmospheric abundances for 70 organic compounds on Titan's upper atmosphere. Concerning the solid phase, we have characterized aerosol analogues synthesized in conditions close to those of Titan's environment, using elemental analysis, pyrolysis, solubility studies and infrared spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Planetary atmosphere; Laboratory simulation; Titan; C<sub>4</sub>N<sub>2</sub>; Aerosol analysis

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### 1. Introduction

The discovery that Titan, the largest satellite of Saturn, has an atmosphere and that methane is a significant constituent of it (Kuiper, 1944), was the starting point for a systematic study of Titan's atmospheric organic chemistry. In the seventies, the interest of the scientific community for Titan was on the increase: a detailed review of the pre-Voyager data on Titan was published by Burns (1977), but the main information on the satellite was obtained from the Voyager encounters in November 1980 (Voyager 1) and 1981 (Voyager 2) (Gehrels and Matthews, 1984; Burns and Matthews, 1986; ESA, 1985). The collected data con-

firmed the presence of an atmosphere, allowed the determination of its vertical temperature and pressure profiles and established the abundance of its main constituents (N<sub>2</sub> and CH<sub>4</sub>). These data also helped to detect several trace constituents. Voyagers data also gave important clues on the hazes and aerosol particles which shroud the surface of the natural satellite. The first suggestion about the complexity of Titan aerosols was made by Sagan, 1974. This new interest for understanding the aerosol's nature increased the number of laboratory studies of complex organic solids produced in N<sub>2</sub>/CH<sub>4</sub> mixtures. With the help of pyrolysis, elemental analysis, and the establishment of optical and spectral properties, several advances have been reached.

Many laboratory simulations of Titan's atmosphere have been carried out, even if several conditions from a real planetary atmosphere cannot be accurately

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reproduced in the laboratory. The lack of realism is particularly due to the absence of vertical temperature and pressure gradients, and to the presence of wall effects. In this sense, laboratory experiments have strong limitations when trying to simulate a real atmosphere. Nevertheless, experimental approaches provide useful information on the nature and relative abundances of trace compounds likely to be present in the studied atmosphere. It is recognized that the solid products formed during the experiments can efficiently mimic the atmospheric aerosols. This is particularly relevant in the case of Titan's tholins. The role of atmospheric particles in the behavior of Titan's atmosphere is so crucial that studies on laboratory analogues of Titan's aerosols are of prime importance. For example observations of the satellite by remote sensing needs to be treated by models, in which optical properties and structure of these atmospheric particles have to be introduced.

With the aid of a simple spark reactor, we demonstrated that results are dependent on the experimental conditions (Coll et al., 1995). For example, Coll et al. (1997) showed that the results obtained by Sagan et al. (1984), Coll et al. (1995) and McKay (1996a) concerning tholins elemental composition are different, and that this variety in the results comes from a significant diversity in tholins production conditions. In fact, it appears that the difference of tholin production modes is a barrier to the complete understanding of the organic aerosol phase of Titan. This difference takes into account:

- the  $\text{CH}_4/\text{N}_2$  ratio in initial gas mixture
- the choice of energy source and its intensity.
- the pressure and temperature of the initial mixture.
- the contamination of the samples by the laboratory atmosphere (presence of oxygen, carbon dioxide and water vapor).

Then, previous laboratory simulations have been unable to accurately reproduce the low temperature and low pressure conditions of Titan's atmosphere. They also suffer from contamination of the highly unstable products from contact with the laboratory atmosphere. This casts uncertainties on the results obtained.

The general aim of the research program developed at LISA is to run simulation experiments under the most realistic possible conditions in the laboratory characterizing the composition of the resulting products in the gaseous and solid phases. The initial obtained information has been reported elsewhere (Vanssay et al., 1995; Coll et al., 1995). We report here the subsequent results, including the protocol description that significantly reduces sample contamination. The acquired data will help us to better understand

the role of the chemical and physical process that take place on Titan.

## 2. Experimental

The reactor developed for this program is a U-tube (Fig. 1, approximately 25 cm high, with an internal diameter of 1.8 cm for the left part and of 0.9 cm for the right part. Iron electrodes are inserted into each end of the tube. They are protected with a mica film to avoid metallization of the reactor. A low pressure flux ( $\approx 2$  mbar of total pressure) of a mixture of  $\text{N}_2/\text{CH}_4$  (98 : 2) passes through the reactor, and a high voltage ( $\approx 4000$  V of direct current, with a circuit internal resistance of 22 k $\Omega$ ) is established between the electrodes. The current raises to  $\approx 80$  mA, and a glow discharge (or cold plasma) is then established inside the reactor (see approximate stream in Fig. 1). The reactor can be immersed in a cryogenic fluid. A cold trap can be added between the output of the reactor and the pumping unit to collect outgoing gases by condensation (Fig. 2). To collect tholins samples, the reactor is put inside a glove box which is filled with nitrogen, then samples are obtained without contamination. The top of the reactor can be opened for introduction of collector plates or for sampling the aerosol analogues.

## 3. Experimental simulation of Titan's atmosphere

The cold plasma reactor described above is submitted to 8 h irradiations. During this time, a volume of  $\text{N}_2\text{-CH}_4$  mixture corresponding to 1.78 mol of gas, or 3.52 mol of (C + N) atoms, moves through the reactor. The temperature of the simulation system was reproducible, but could not be directly measured. However, we have determined that it was in the range of 100–150 K, and was maintained constant during each experiment. The deposited energy was determined using an actinometry method based on  $\text{C}_2\text{H}_4$  irradiation, which gives rise to  $\text{C}_2\text{H}_2$ ,  $\text{H}_2$  and  $\text{CH}_4$ . There is a known correlation between the  $\text{C}_2\text{H}_2$  yield (molecules/100 eV) and the pressure of  $\text{C}_2\text{H}_4$  (Sauer and Dorfman, 1961). In this way we were able to estimate the energy deposited to the reactant gas mixture, at 1.5 mbar, to be  $9 \times 10^{24}$  eV.

The mixture of gases formed during experimental simulation was analyzed: 44 hydrocarbons and 26 N-containing compounds were identified by GC-MS during a run (Table 1). Using the energy value of  $9 \times 10^{24}$  eV and considering the quantities detected during gas mixture analysis, we can calculate the production yield of each gaseous product, in molecules/100 eV. Therefore, we can deduce the total production

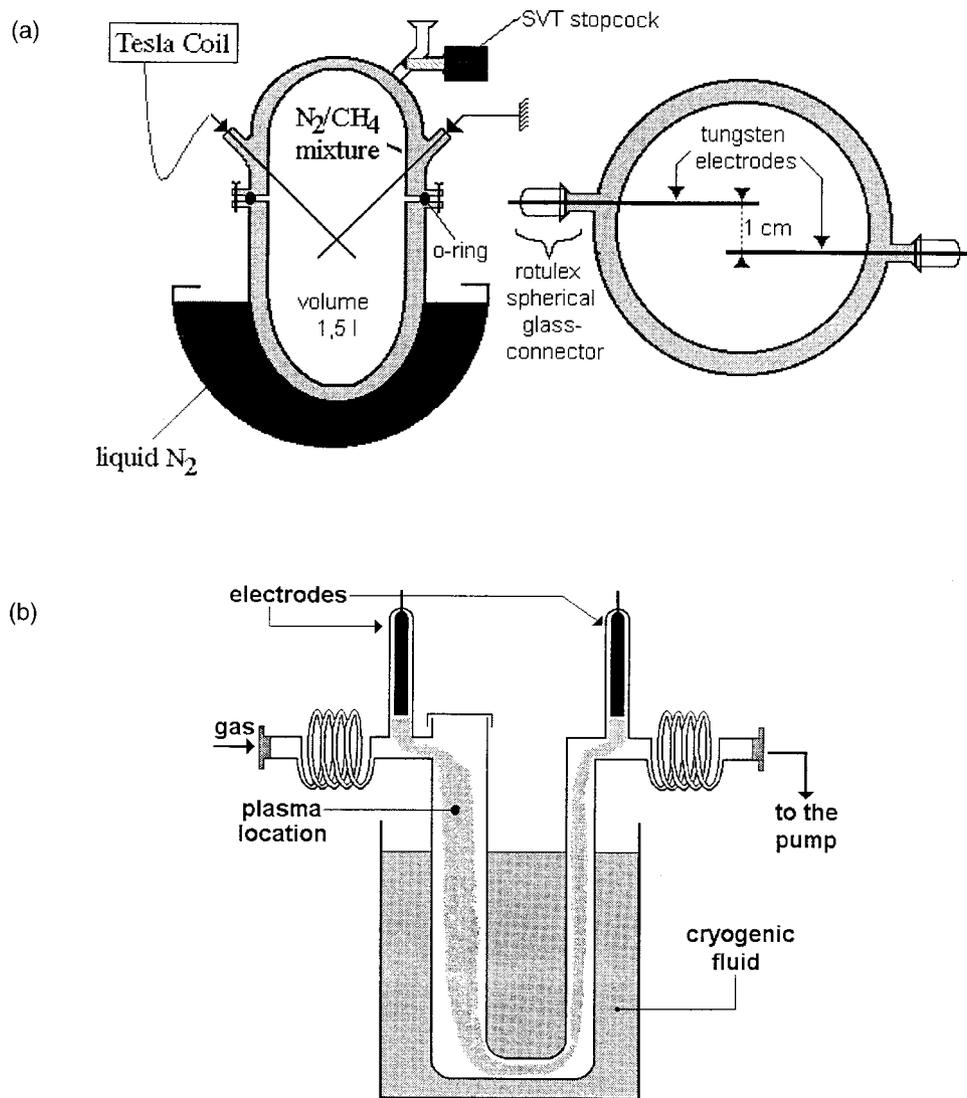


Fig. 1. Reactors developed at LISA for experimental simulations of Titan's atmosphere. (a) reactor used for spark discharge at low temperature. (b) reactor used for plasma discharge at low temperature.

yield  $G_{\text{total}}$ , which corresponds to  $\sum_i(n_C + n_N)G_i$ , where  $i$  is a gaseous species,  $(n_C + n_N)$  the total number of C and N atoms, and  $G_i$  the production yield of the species.  $G_{\text{total}}$  is 1.04 atom/100 eV, which means that only 4.4% of the heavy atom content of the initial mixture has been integrated into the products.

#### 4. Extrapolation to Titan's atmospheric composition

Our results have been extrapolated to Titan conditions using a simple atmospheric mixing model, adapted from a similar work (Thompson et al., 1991). The production yields  $G_i$  are used to calculate production fluxes in Titan's upper atmosphere. We consider that each compound, produced at high altitude, mixes downward through several scale heights  $H$ , and

is removed at its condensation altitude (Thompson et al., 1991). We have used updated values of parameters: in particular the eddy diffusion profile was adjusted (Toublanc et al., 1995) in order to fit the mean vertical distribution of HCN retrieved from millimeter ground based observations (Tanguy et al., 1990). The obtained minimum eddy diffusion value is  $2 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$  at  $\approx 112 \text{ km}$ . The quantitative predictions on Titan of the simulation detected compounds abundances are reported in Table 1. A comparison between our predicted abundances to the observed and photochemical proposed ones (Toublanc et al., 1995; Yung et al., 1984) is shown in Fig. 3. The ten displayed compounds correspond to that observed on Titan by Voyager I.

The plasma used as the energy source in these experiments reproduces the chemistry initiated by the high energy particles of Titan's atmosphere (Scattergood et

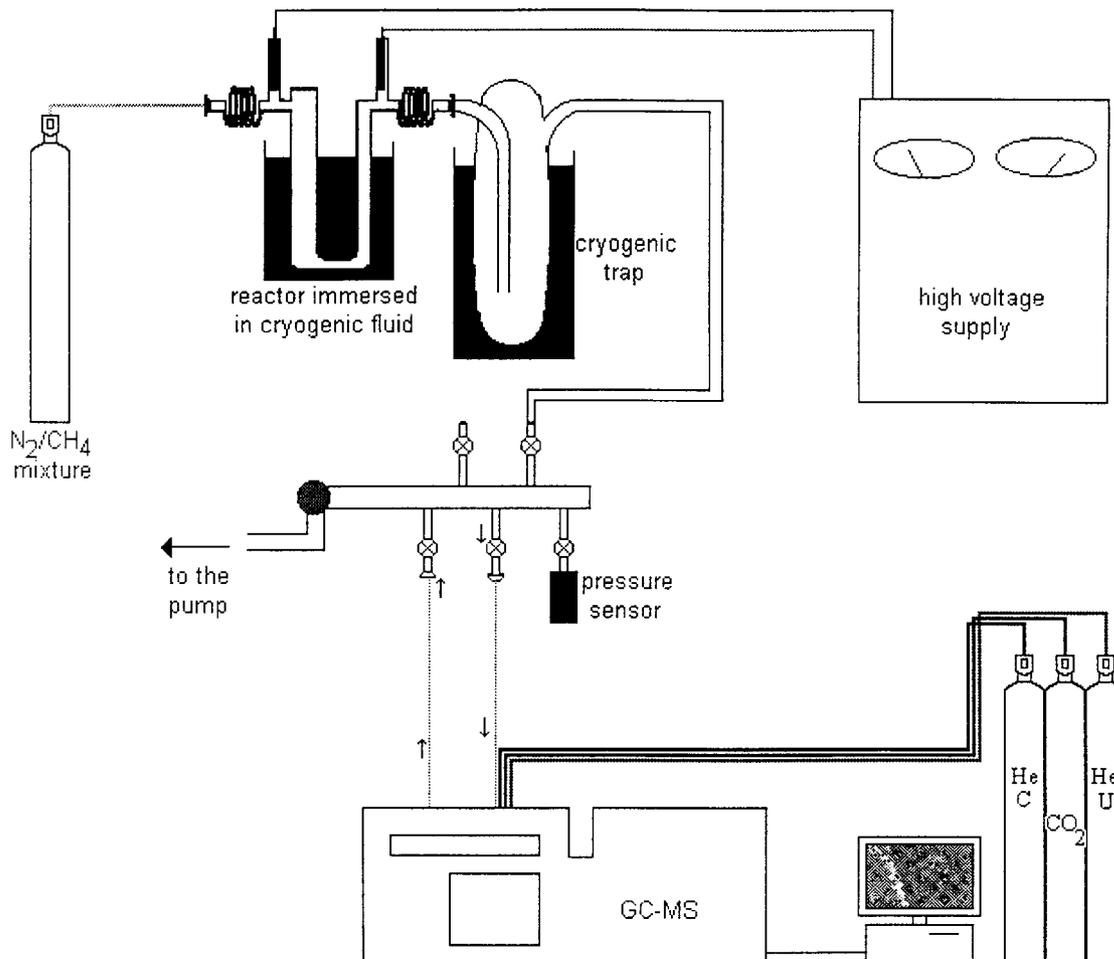


Fig. 2. Experiment devoted to qualitative and quantitative studies of gaseous compounds produced during the laboratory simulations of Titan's atmosphere (analysis by gas phase chromatograph coupled with mass spectrometry).

al., 1989). This plasma emits UV–Vis light which intensity and wavelengths are unknown. On the other hand, it is commonly accepted that only solar UV radiation with wavelengths  $< 100$  nm is capable of dissociating the  $N_2$  molecule, and that higher wavelengths induce primary products chemistry. To estimate the impact of the UV radiation in our results, we develop at present ultraviolet spectrophotometry measurements of the plasma.

Our calculations use an energy flux which corresponds to an irradiation by high energy particles and does not consider the contribution from the flux of photons. Thus, the mixing ratios for  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$  and  $C_3H_8$  are, unsurprisingly, underestimated, as these species are primary products of photochemistry processes. On the contrary, our predictions concerning the mixing ratios of HCN,  $C_3H_4$ ,  $HC_3N$ ,  $CH_3CN$  and  $C_2N_2$  are in the range of the observations, although  $C_4H_2$  is slightly low. Photochemical models are more able to reproduce abundances of primary photochemical products, but overestimate the mixing ratios of

other species ( $HCN$ ,  $C_3H_4$ ,  $C_4H_2$ ,  $HC_3N$  and  $C_2N_2$ ). This contradiction proves that only experimental simulations can effectively predict the abundances of minor compounds. To accomplish the same task, modeling studies require knowledge of the entire chemical scheme of an atmosphere, with all associated rate constant values and branching ratios.

Among the detected species, it is important to notice the presence of uncommon compounds, such as  $C_6H_2$ ,  $HC_5N$  and  $C_4N_2$ . The first two have only recently been detected in experimental simulations (Vanssay et al., 1995; Coll et al., 1995). Their identification, with the help of standard samples mass spectra, confirms the formation of polyynes ( $C_{2n}H_2$ ) and cyanopolyynes ( $HC_{2n+3}N$ ) in such high energetic particle irradiations. Exobiological implications of these compounds have been described elsewhere (Vanssay et al., 1995; Raulin et al., 1996). Until now solid  $C_4N_2$  is the only trace constituent of Titan's atmosphere that rested without being observed in previous simulation experiments (Khanna et al., 1987). On Titan, it can be

Table 1

Computed values on Titan of the column densities  $N_i$  (molecules/cm<sup>-2</sup>) and mole fractions  $X_i$  of each organic compound detected during simulation experiments of Titan's atmosphere

Gross formula	Species	$N_1$ (min)	$N_1$ (max)	$X_1$ (min)	$X_1$ (max)
C <sub>2</sub> H <sub>2</sub>	Ethyne	5.0E+17	2.5E+18	9.9E-08	4.9E-07
HCN	Methanenitrile	8.4E+16	4.2E+17	2.9E-08	1.5E-07
C <sub>2</sub> H <sub>6</sub>	Ethane	2.8E+16	1.4E+17	3.9E-09	1.9E-08
C <sub>3</sub> H <sub>8</sub>	Propane	6.9E+15	3.4E+16	1.5E-09	7.7E-09
C <sub>3</sub> H <sub>4</sub>	Propyne	6.6E+15	3.3E+16	1.4E-09	7.2E-09
C <sub>2</sub> H <sub>4</sub>	Ethene	1.1E+16	5.3E+16	4.7E-10	2.4E-09
C <sub>4</sub> H <sub>10</sub>	Methylpropane	8.4E+14	4.2E+15	2.4E-10	1.2E-09
C <sub>3</sub> H <sub>6</sub>	Propene	1.1E+15	5.7E+15	2.2E-10	1.1E-09
C <sub>4</sub> H <sub>10</sub>	Butane	7.0E+14	3.5E+15	2.0E-10	1.0E-09
HC <sub>3</sub> N	Propynenitrile	4.1E+14	2.1E+15	1.6E-10	8.0E-10
C <sub>3</sub> H <sub>4</sub>	Propadiene	4.2E+14	2.1E+15	9.1E-11	4.6E-10
C <sub>3</sub> H <sub>5</sub> N	Propanenitrile	1.9E+14	9.7E+14	8.1E-11	4.1E-10
C <sub>6</sub> H <sub>6</sub>	Benzene	1.0E+14	5.2E+14	6.6E-11	3.3E-10
C <sub>4</sub> H <sub>2</sub>	Buta-1,3-diyne	2.0E+14	1.0E+15	6.4E-11	3.2E-10
C <sub>5</sub> H <sub>12</sub>	Methyl-2-butane	1.5E+14	7.7E+14	6.0E-11	3.0E-10
CH <sub>3</sub> CN	Ethanenitrile	1.8E+14	9.1E+14	5.7E-11	2.9E-10
C <sub>4</sub> H <sub>8</sub>	But-2-ene	1.9E+14	9.7E+14	4.7E-11	2.3E-10
C <sub>3</sub> H <sub>3</sub> N	Propenenitrile	8.9E+13	4.4E+14	4.0E-11	2.0E-10
C <sub>7</sub> H <sub>8</sub>	Toluene	1.6E+13	8.2E+13	3.4E-11	1.7E-10
C <sub>2</sub> N <sub>2</sub>	Ethanedinitrile	1.0E+14	5.2E+14	3.0E-11	1.5E-10
C <sub>6</sub> H <sub>14</sub>	Dimethyl-2,2-butane	3.3E+13	1.6E+14	2.9E-11	1.5E-10
C <sub>7</sub> H <sub>16</sub>	Heptane	1.2E+13	5.9E+13	2.5E-11	1.2E-10
C <sub>5</sub> H <sub>12</sub>	Pentane	5.6E+13	2.8E+14	2.2E-11	1.1E-10
C <sub>6</sub> H <sub>14</sub>	Methyl-3-pentane	2.3E+13	1.1E+14	2.0E-11	1.0E-10
C <sub>6</sub> H <sub>14</sub>	Hexane	1.8E+13	9.1E+13	1.6E-11	8.1E-11
C <sub>4</sub> H <sub>8</sub>	But-1-ene	6.7E+13	3.3E+14	1.6E-11	8.1E-11
C <sub>6</sub> H <sub>14</sub>	Methyl-2-pentane	1.8E+13	8.9E+13	1.6E-11	8.0E-11
C <sub>4</sub> H <sub>4</sub>	But-1-ene-3-yne	6.1E+13	3.0E+14	1.5E-11	7.3E-11
C <sub>4</sub> H <sub>8</sub>	Methylprop-2-ene	5.8E+13	2.9E+14	1.4E-11	7.0E-11
C <sub>4</sub> H <sub>6</sub>	But-2-yne	5.3E+13	2.7E+14	1.4E-11	7.0E-11
C <sub>4</sub> H <sub>6</sub>	Buta-1,3-diene	5.2E+13	2.6E+14	1.4E-11	6.8E-11
C <sub>5</sub> H <sub>9</sub> N	Dimethyl-2,2-propanenitrile	1.5E+13	7.3E+13	1.3E-11	6.6E-11
C <sub>5</sub> H <sub>12</sub>	Dimethylpropane	3.3E+13	1.7E+14	1.2E-11	5.8E-11
C <sub>4</sub> H <sub>7</sub> N	Methyl-2-propanenitrile	2.1E+13	1.1E+14	1.1E-11	5.6E-11
C <sub>4</sub> H <sub>6</sub>	Buta-1,2-diene	3.1E+13	1.5E+14	8.0E-12	4.0E-11
C <sub>6</sub> H <sub>14</sub>	Dimethyl-2,3-butane	8.0E+12	4.0E+13	7.2E-12	3.6E-11
CH <sub>3</sub> N <sub>3</sub>	Methylazide?	1.5E+13	7.5E+13	6.8E-12	3.4E-11
CH <sub>3</sub> NC	Isocyanide?	2.0E+13	1.0E+14	6.4E-12	3.2E-11
C <sub>4</sub> H <sub>7</sub> N	Butanenitrile	1.1E+13	5.3E+13	5.6E-12	2.8E-11
C <sub>5</sub> H <sub>10</sub>	Pent-2-ene	1.6E+13	8.2E+13	4.5E-12	2.2E-11
C <sub>4</sub> H <sub>6</sub>	But-1-yne	1.7E+13	8.5E+13	4.4E-12	2.2E-11
C <sub>3</sub> H <sub>6</sub>	Cyclopropane	2.1E+13	1.1E+14	4.2E-12	2.1E-11
C <sub>4</sub> H <sub>5</sub> N	But-2-enenitrile	7.9E+12	4.0E+13	4.2E-12	2.1E-11
C <sub>4</sub> H <sub>3</sub> N	But-2-ynenitrile	5.5E+12	2.8E+13	2.9E-12	1.4E-11
C <sub>5</sub> H <sub>10</sub>	Methyl-2-but-1-ene	1.0E+13	5.1E+13	2.8E-12	1.4E-11
C <sub>4</sub> H <sub>8</sub>	Cyclobutane	7.6E+12	3.8E+13	1.8E-12	9.1E-12
C <sub>5</sub> H <sub>10</sub>	Methyl-3-but-2-ene	5.3E+12	2.6E+13	1.4E-12	7.2E-12
C <sub>5</sub> H <sub>10</sub>	Methyl-3-pent-1-ene	5.3E+12	2.6E+13	1.4E-12	7.2E-12
C <sub>5</sub> H <sub>10</sub>	Pent-1-ene	5.1E+12	2.5E+13	1.4E-12	6.9E-12
C <sub>4</sub> H <sub>5</sub> N	But-3-enenitrile	2.4E+12	1.2E+13	1.3E-12	6.4E-12
C <sub>5</sub> H <sub>10</sub>	Cyclopentane	4.0E+12	2.0E+13	1.1E-12	5.5E-12
C <sub>4</sub> H <sub>5</sub> N	Methyl-2-butenenitrile	1.8E+12	9.2E+12	9.6E-13	4.8E-12
C <sub>5</sub> H <sub>9</sub> N	Pentanenitrile	1.0E+12	5.2E+12	9.4E-13	4.7E-12
C <sub>5</sub> H <sub>7</sub> N	Pent-2-enenitrile	1.3E+12	6.5E+12	8.2E-13	4.1E-12
C <sub>5</sub> H <sub>7</sub> N	Methyl-2-but-2-enenitrile	9.8E+11	4.9E+12	6.2E-13	3.1E-12
C <sub>5</sub> H <sub>7</sub> N	Methyl-3-but-2-enenitrile	9.8E+11	4.9E+12	6.2E-13	3.1E-12
C <sub>6</sub> H <sub>2</sub>	Hexatriyne	9.8E+11	4.9E+12	6.2E-13	3.1E-12
C <sub>6</sub> H <sub>7</sub> N	Unidentified	2.2E+11	1.1E+12	4.7E-13	2.3E-12
C <sub>5</sub> H <sub>7</sub> N	Pent-4-enenitrile	6.5E+11	3.3E+12	4.1E-13	2.1E-12

(continued on next page)

Table 1 (continued)

Gross formula	Species	$N_1$ (min)	$N_1$ (max)	$X_1$ (min)	$X_1$ (max)
C <sub>5</sub> H <sub>8</sub>	Penta-1,3-diene	1.2E+12	6.2E+12	3.0E-13	1.5E-12
C <sub>5</sub> H <sub>8</sub>	Penta-2,3-diene	1.1E+12	5.3E+12	2.5E-13	1.3E-12
C <sub>5</sub> H <sub>5</sub> N	Penta-2,4-dienitrile	3.3E+11	1.6E+12	2.1E-13	1.0E-12
C <sub>5</sub> H <sub>7</sub> N	Methyl-2-but-3-enitrile	3.3E+11	1.6E+12	2.1E-13	1.0E-12
C <sub>5</sub> H <sub>6</sub>	Cyclopentadiene	8.7E+11	4.4E+12	1.9E-13	9.4E-13
C <sub>5</sub> H <sub>6</sub>	Pent-2-yne-4-ene	8.7E+11	4.4E+12	1.9E-13	9.4E-13
C <sub>5</sub> H <sub>6</sub>	Pent-1-yne-3-ene	7.3E+11	3.6E+12	1.6E-13	7.9E-13
HC <sub>5</sub> N	Pentadiynitrile	2.8E+11	1.4E+12	1.3E-13	6.4E-13
C <sub>5</sub> H <sub>8</sub>	Methyl-3-but-1-yne	5.3E+11	2.6E+12	1.3E-13	6.4E-13
C <sub>5</sub> H <sub>7</sub> N	Pent-3-enitrile	1.6E+11	8.2E+11	1.0E-13	5.1E-13
C <sub>1</sub> N <sub>2</sub>	Butynedinitrile	6.1E+08	3.1E+09	2.1E-16	1.1E-15

produced by the following mechanism, which is driven by the presence of N atoms in the high atmosphere:



The CHCN can then react in one of two ways:



The formation of C<sub>4</sub>N<sub>2</sub> from CN and HC<sub>3</sub>N (Yung, 1987) is negligible compared to this mechanism (Halpern et al., 1989). Comparison of a Titan's limb spectrum with laboratory spectra of both solid and gaseous C<sub>4</sub>N<sub>2</sub> have been made (Samuelson and Mayo,

1991), indicating an upper limit for the mole fraction of gaseous C<sub>4</sub>N<sub>2</sub> of  $4 \times 10^{-10}$ . This is compatible with the upper limit derived from recent infrared studies of C<sub>4</sub>N<sub>2</sub> (Khlifi et al., 1997). Our prediction, based on simulation results, is a mole fraction for gaseous C<sub>4</sub>N<sub>2</sub> of  $2 \times 10^{-16}$  to  $1 \times 10^{-15}$  (Table 1). These values are probably lower than the real abundance, because of the great instability of this compound (Aflalaye et al., 1995). Even with synthesis under low temperature conditions and analysis with a fast gas-phase chromatography system, the quantity of C<sub>4</sub>N<sub>2</sub> detected is always very low, and independent of the irradiation time. We can conclude that the detected quantity is lower than the formed one, and that the value of  $1 \times 10^{-15}$  is a lower limit for the abundance of this compound on Titan.

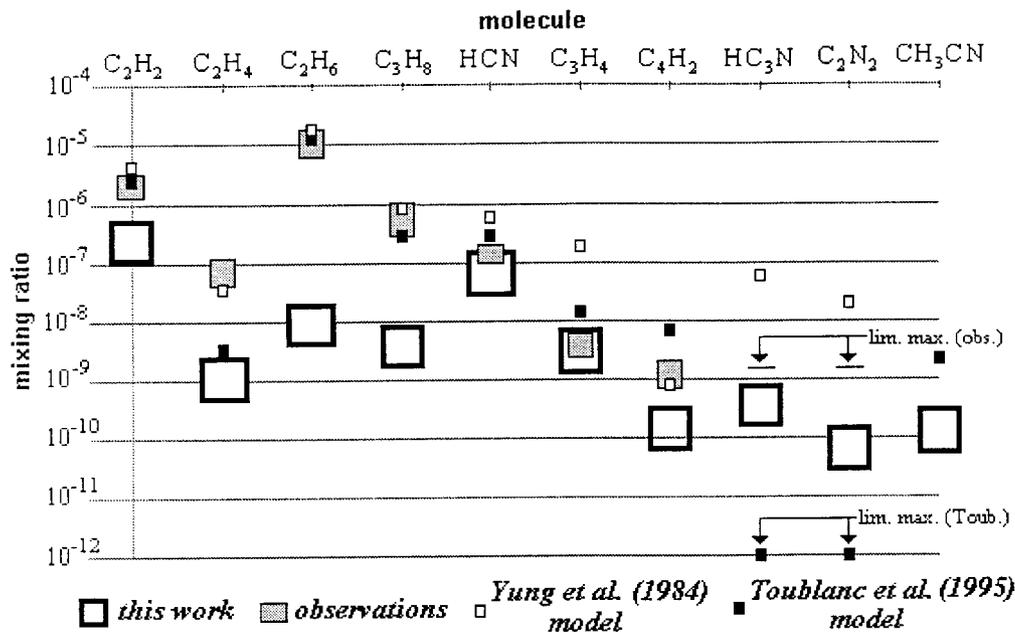


Fig. 3. Comparison of mixing ratios of 10 organic compounds on Titan: 1) from extrapolation of this work (squares represent uncertainties in calculated values) 2) determined from observations (squares represent uncertainties in observational data) 3) predicted by 2 photochemical models.

## 5. Synthesis of aerosol analogues (tholins)

The solid phase synthesized during the simulation experiments is an analogue of the solid aerosol particles produced in Titan's upper atmosphere, and is usually referred to as 'tholins'. We have carried out several analyses of these products, synthesized at low temperature, and with care taken to avoid any atmospheric contamination during production and sample analysis. We carried out an elemental analysis of these products, which gave us a C/N ratio in the range of 2.82–2.83, and a C/H ratio in the range of 0.79–0.8. Such characterization of laboratory tholins have been made previously (Coll et al., 1995; Coll et al., 1997; McKay, 1996a; Sagan et al., 1984;). Sagan et al. (1984) found a C/N ratio of 1.93 for tholins synthesized with a continuous flow system (10% CH<sub>4</sub>) at low pressure and room temperature, Coll et al. (1995) obtained a C/N ratio of 11 for tholins synthesized at high pressure and low temperature in a static mixture (10% CH<sub>4</sub>), and Coll et al. (1997) found a ratio of 1.73 under conditions similar to those of Sagan et al. (1984), but with a 2% CH<sub>4</sub> mixture. McKay (1996a) found a C/N ratio of 5 in tholins synthesized at room temperature and high pressure with a continuous flow system. These results establish that the C/N ratio increases with pressure and/or low temperature. Our latest results, corresponding to a gross formula of (C<sub>11</sub>N<sub>4</sub>H<sub>14</sub>)<sub>n</sub>, obtained at low temperature and low pressure, with a reactant mixture of realistic composition, are the most representative of Titan's environment ever used in the laboratory. These ratios can, therefore, be considered as representative of the elemental composition of Titan's aerosols. As emphasized in some works (McKay, 1996a), Titan's organic haze is potentially an

important sink of photochemically produced carbon and nitrogen compounds. Bar-Nun and Podolak (1979) suggested a rate of material production  $\approx 2.5 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ . Today, an assortment of microphysical haze models all confirm that the haze production rate is  $1 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ , within a factor of two. If we consider our gross formula, the haze production represents a sink for C of  $3 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$ , and a sink for N of  $1 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$ . The haze is a small sink for C atoms compared to condensation of hydrocarbons, but the sink for N is comparable to the total production rate of HCN (McKay, 1996b) and must be considered significant.

## 6. Structural analysis of tholins

The tholins were also characterized by their infrared spectrum. Only qualitative analyses have been carried out in this work, revealing many chemical structures in the product (Fig. 4). Comparing our tholins spectrum to that of the tholins synthesized at Cornell University, by the Carl Sagan team (McDonald et al., 1994), we encountered some differences. Under the assumption of a product composed only by C, N and H, we tried to interpret the features in our spectrum, but the designation of a characteristic absorbing chemical group for each one of the displayed bands is quite difficult, except for the one at  $2182 \text{ cm}^{-1}$ , which can be clearly identify as the  $\text{C} \equiv \text{N}$  stretching band. Some contradictions between different band series seem to prove that tholins are composed of an aggregation of many products. It is easier to compare the tholin spectrum with infrared spectra of known compounds, which may play a key role in aerosol for-

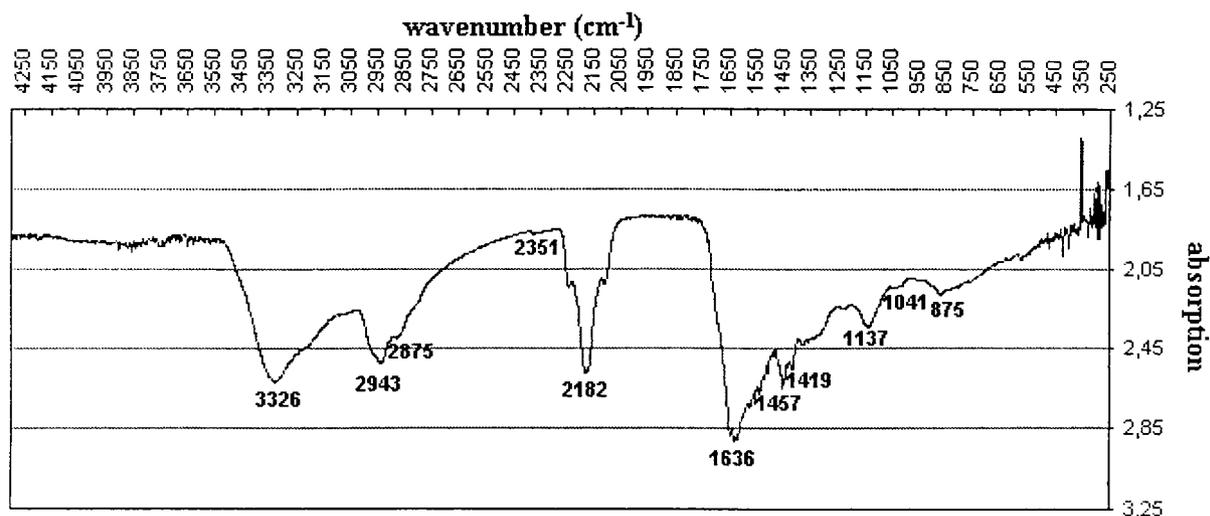


Fig. 4. Infrared spectrum of tholin synthesized at low temperature.

mation. We have made comparisons with spectra of  $\text{HC}_3\text{N}$  polymers,  $\text{HC}_3\text{N}/\text{C}_2\text{H}_6$  and  $\text{HC}_3\text{N}/\text{C}_2\text{H}_2$  polymers and with spectra of different poly-HCN compounds (Clarke and Ferris, 1997). Taking into account the vast work of C.N. Matthews on HCN and poly-HCN (Matthews, 1992), we noticed that only the spectra of poly-HCN, prepared under anhydrous conditions, have a similar appearance with our tholin spectra (Völker, 1960). Of course, the C/N ratio of 2.83 shows that tholins are not pure poly-HCN, but the infrared spectrum suggests that the base of tholins could be poly-HCN.

Another way to study the chemical structure of tholins is by their pyrolysis. In the frame of the Cassini–Huygens mission, pyrolysis-GC-MS of tholins have been carried out, using a special instrument: a prototype of the Huygens ACP experiment (Aerosol Collector Pyrolyser, PI: Guy Israël, Service d'Aéronomie du C.N.R.S., 1997). Under the chosen conditions (Coll et al., 1997), analysis of our tholins yielded 27 hydrocarbons and 19 nitriles (see Table 2). It appears that these two families of compounds dominate the composition of tholins. The principal difference between this analysis and previous works (Khare et al., 1984; Ehrenfreund et al., 1995) is the absence of aromatic or cyclic compounds other than benzene. Does this mean that tholins are poor in cyclic compounds? Or could benzene be the main pyrolysis product of PAH's? Interpreting programs can be difficult,

but they are essentially a fingerprint of the pyrolysed compound. By producing various tholins in the laboratory, under different conditions, a library of 'fingerprints' could be built up. With future data from the ACP experiment this would become a powerful tool in identifying the nature of Titan's aerosols.

## 7. Observation of tholins

We have also viewed tholins with the help of an electron microscopy (MEB). The first observed samples were tholins synthesized at room temperature, and they appeared as a yellow powder. This powder showed a quasi-homogeneous distribution of  $1\ \mu\text{m}$  particles, each particle consisting of an aggregation of 100 nm spheres. Tholins synthesized at low temperature were found to be semi-liquid and very dark in color. We could not elucidate the structure of these compounds, but we could observe tholins dissolved in liquid nitriles, like acetonitrile (Fig. 5). They reveal bunches of  $\approx 0.3\ \mu\text{m}$  spheres. This mean diameter is in the usual range of such products (see Bar-Nun et al., 1988; Scattergood et al., 1992; Vanssay, 1994) and this observation of tholins is compatible with a two-stage growth of aerosol:

1. initial growth of aerosols near the formation altitude by accretion of very small elementary particles

Table 2  
Pyrolysates table of tholins

Hydrocarbons	Gross formula and abundance	Nitrogened compounds	Gross formula and abundance
Several $\text{C}_2$	$\text{C}_2\text{H}_y$ , 21.05%	Cyanhydric acid	HCN, 28.01%
Benzene	$\text{C}_6\text{H}_6$ , 2.75%	Acetonitrile	$\text{CH}_3\text{CN}$ , 25.87%
Propene	$\text{C}_3\text{H}_6$ , 2.02%	Dimethyl-3,3-cyclobutane-carbonitrile	$\text{C}_7\text{H}_{11}\text{N}$ , 4.38%
Propane	$\text{C}_3\text{H}_8$ , 1.63%	Dicarbonitrile-cyclobutane	$\text{C}_6\text{H}_6\text{N}_2$ , 2.77%
Toluene	$\text{C}_7\text{H}_8$ , 1.61%	Cyanomethane	$\text{CH}_3\text{NC}$ , 2.71%
But-1-ene	$\text{C}_4\text{H}_6$ , < 1%	$\text{C}_4$ nitrile	$\text{C}_3\text{H}_x\text{CN}$ , 1.29%
Buta-1,3-diene	$\text{C}_4\text{H}_6$ , < 1%	Butanenitrile	$\text{C}_4\text{H}_7\text{N}$ , 1.11%
But-2-ene <i>trans</i>	$\text{C}_4\text{H}_8$ , < 1%	Undetermined	$\text{C}_x\text{H}_y\text{H}_z$ , < 1%
But-2-ene <i>cis</i>	$\text{C}_4\text{H}_8$ , < 1%	$\text{C}_4$ nitrile	$\text{C}_3\text{H}_x\text{CN}$ , < 1%
Methyl-2-propane	$\text{C}_4\text{H}_{10}$ , < 1%	Isocyano-1-propane	$\text{C}_4\text{H}_7\text{N}$ , < 1%
$\text{C}_4$ hydrocarbobb	$\text{C}_4\text{H}_x$ , < 1%	cyanogen	$\text{C}_2\text{N}_2$ , < 1%
Butane	$\text{C}_4\text{H}_{10}$ , < 1%	Undetermined	$\text{C}_x\text{H}_y\text{N}_z$ , < 1%
Pent-2-ene	$\text{C}_5\text{H}_{10}$ , < 1%	Undetermined	$\text{C}_x\text{H}_y\text{N}_z$ , < 1%
substitued benzene	$\text{C}_x\text{H}_y$ , < 1%	Dimethyl-2,3-butanedinitrile	$\text{C}_6\text{H}_8\text{N}_2$ , < 1%
Dimethyl-1,4 benzene	$\text{C}_8\text{H}_{10}$ , < 1%	Nitrile en $\text{C}_5$	$\text{C}_4\text{H}_x\text{CN}$ , < 1%
Dimethyl-1,3-benzene	$\text{C}_8\text{H}_{10}$ , < 1%	Methylene-2-butanenitrile	$\text{C}_5\text{H}_7\text{N}$ , < 1%
But-1-ene-yne	$\text{C}_4\text{H}_4$ , < 1%	Undetermined	$\text{C}_x\text{H}_y\text{N}_z$ , < 1%
Hepta-1,2-diene	$\text{C}_7\text{H}_{12}$ , < 1%	Pentanedinitrile	$\text{C}_5\text{H}_6\text{N}_2$ , < 1%
Pentyne	$\text{C}_5\text{H}_8$ , < 1%	Pentanenitrile	$\text{C}_5\text{H}_9\text{N}$ , 1%
Pentane	$\text{C}_5\text{H}_{12}$ , < 1%	Propenenitrile	$\text{C}_3\text{H}_3\text{N}$ , < 1%
Methyl-1-ethyl-3-benzene	$\text{C}_9\text{H}_{12}$ , < 1%		
Methyl-1-ethyl-4-benzene	$\text{C}_9\text{H}_{12}$ , < 1%		
Pent-1-ene	$\text{C}_5\text{H}_{10}$ , < 1%		
Ethenyl-benzene	$\text{C}_8\text{H}_8$ , < 1%		
Trimethyl-x, x, x-benzene	$\text{C}_9\text{H}_{12}$ , < 1%		

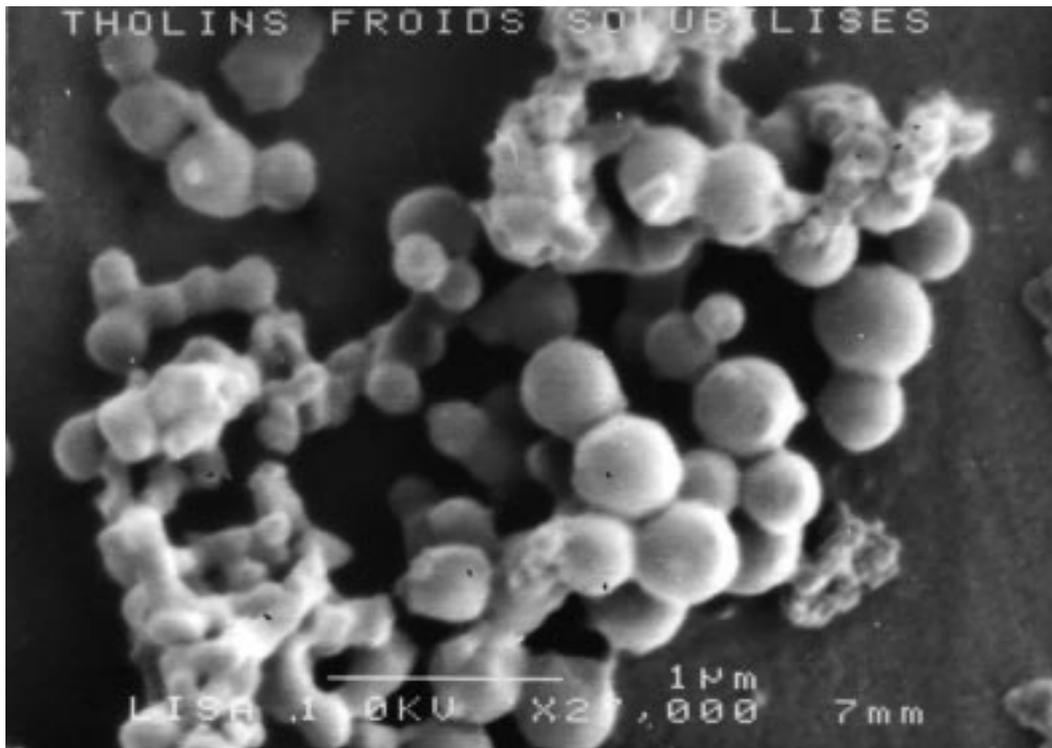


Fig. 5. Electron microscopy observations of tholins dissolved in nitriles (main scale bar = 1  $\mu\text{m}$ ).

2. settling, at this stage particles of about the same size stick together leading to the formation of aggregates which contain tens of monomers (Cabane et al., 1992).

### 8. Solubility of tholins

We also carried out solubility studies of tholins in liquid hydrocarbons and nitriles. We confirm the results on their insolubility in hydrocarbons (McKay, 1996a), concluding that little or no polymeric organic material is dissolved in Titan's hydrocarbon lakes or ponds. Contrasting, tholins are soluble in nitriles. At room temperature, we observe the following saturation concentrations of tholins:

- 4.0  $\text{mg ml}^{-1}$  in acetonitrile
- 6.0  $\text{mg ml}^{-1}$  in isobutyronitrile
- 5.5  $\text{mg ml}^{-1}$  in propionitrile
- 8.0  $\text{mg ml}^{-1}$  in benzonitrile

This solubility in nitriles has important implications, because it suggests that the tholins have small contact angles with nitriles (mainly HCN), contrary to hydrocarbons. Thus, nitriles should easily condense on aerosol nuclei. This has important implications for the study of nitrile species and the surface properties of the aerosols.

### 9. Conclusion

We have reported here the development of a laboratory experimental simulation program of Titan's atmosphere. The main goal is to demonstrate the importance of the use of experimental parameters in atmospheric modeling, as emphasized by Sagan et al. (1992) and McKay (1996a). We have detected gaseous  $\text{C}_4\text{N}_2$  for the first time and this discovery proves that our experimental parameters represent Titan's atmosphere with sufficient accuracy. We have also proved that it is possible to extrapolate the results of a laboratory experiment to a planetary atmosphere. Thus, we propose mole fractions for 70 compounds and find a good agreement with observed values. Aerosol analogues formed under our appropriate and well-controlled conditions appeared as dark semi-liquid oligomers, which we have investigated at a microscopic scale. For the first time a tholins stoichiometric formula has been determined, with an upper limit for oxygen atom contamination of 1 : 150 atoms, which is considerably lower than previous studies ( $\approx 1 : 15$  atoms). This stoichiometry corresponds to a  $(\text{C}_{11}\text{N}_4\text{H}_{14})_n$  gross formula, revealing that aerosols are an important sink for N atoms on Titan. We have suggested that tholins may be partially composed of poly-HCN, and have established that tholins are soluble in nitriles.

## 10. Future work

In the experimental development of the program, we have to determine the photolysis wavelength and rate inside the plasma, because UV photolysis plays a major role for Titan's chemistry. Then, we have to adjust this parameter to the real conditions.

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