Transition from Gaseous Compounds to Aerosols in Titan's Atmosphere

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We investigate the chemical transition of simple molecules like C_2H_2 and HCN into aerosol particles in the context of Titan's atmosphere. Experiments that synthesize analogs (tholins) for these aerosols can help illuminate and constrain these polymerization mechanisms. Using information available from these experiments, we suggest chemical pathways that can link simple molecules to macromolecules, which will be the precursors to aerosol particles: polymers of acetylene and cyanoacetylene, polycyclic aromatics, polymers of HCN and other nitriles, and polyynes. Although our goal here is not to build a detailed kinetic model for this transition, we propose parameterizations to estimate the production rates of these macromolecules, their C/N and C/H ratios, and the loss of parent molecules (C_2H_2, HCN, HC_3N and other nitriles, and C_6H_6) from the gas phase to the haze. We use a one-dimensional photochemical model of Titan's atmosphere to estimate the formation rate of precursor macromolecules. We find a production zone slightly lower than 200 km altitude with a total production rate of 4×10^{-14} g cm^{-2} s^{-1} and a C/N $\simeq$ 4. These results are compared with experimental data, and to microphysical model requirements. The Cassini/Huygens mission will bring a detailed picture of the haze distribution and properties, which will be a great challenge for our understanding of these chemical processes.

Key Words: **Titan; photochemistry; organic chemistry; atmospheric, composition.**

1. INTRODUCTION

The dense atmosphere of Titan is composed of approximately 98% nitrogen molecules and 2% methane. Photochemistry occurring in this atmosphere yields a suite of other gaseous compounds, including hydrocarbons and nitriles (e.g., ethane and hydrogen cyanide). An aerosol layer, which hides Titan's surface in visible light, is also present in the stratosphere. The composition of the gas and the microphysics of the haze have been studied through observations (both ground-based and from the Voyager spacecrafts) and modeling. But the formation of this haze, from photochemical processes in the gas phase to the smallest aerosol particles considered in the microphysical models (which we will call "precursors") is not well understood. Photochemical models (Yung *et al.* 1984, Toublanc *et al.* 1995, Lara *et al.* 1996, Lebonnois *et al.* 2001) do not follow the fate of gaseous compounds with more than six heavy atoms (C and N), while microphysical models (McKay *et al.* 1989, Toon *et al.* 1992; Rannou *et al.* 1995, 1997) assume the existence of small particles (of radius around 13 Å) as the source of material and then follow the microphysical evolution of the particles while conserving mass. Only one study has been done to detail the chemistry of hydrocarbons up to C_{60} macromolecules (Dimitrov and Bar-Nun 1997), but this work does not include N-bearing species and has not yet been applied to simulate Titan's atmospheric composition. In Dimitrov and Bar-Nun (1999), the authors present a model of the agglomeration of aerosols that uses this study. Their model can well reproduce the laboratory synthesis of aerosol particles from Bar-Nun *et al.* (1988). It was also applied to describe a possible scenario for the synthesis of Titan's aerosols, but no direct comparison was made with observations or with other detailed microphysical models (e.g., Toon *et al.* 1992, Rannou *et al.* 1995, 1997).

In this paper, we address the question of how to link photochemical models to microphysical models in a simple, parameterized way, without including a detailed kinetic model to describe all reactions involved in macromolecule formation. In order to couple these two kinds of models, it is necessary to quantify the production rate of precursors from photochemical reactions and to evaluate the chemical loss of gas phase molecules to the haze. This does not concern the possible condensation of gas phase molecules on aerosol particles in the low stratosphere and troposphere (typically 40 to 150 km altitude). This is a problem that needs to be treated in the microphysical models and that does not affect the source function of the haze. In the microphysical models, no addition of mass from the gas phase is considered, which means that chemical growth of macromolecules with addition of gas phase small molecules (e.g., C_2H_2, HCN, HC_3N) is assumed negligible when the smallest aerosol particles are considered. We will call this transition the precursor level.

The principles adopted in this paper are the following:

- Given a set of chemical species included in the photochemical model, the production of aerosols occurs through a set of initial reactions that will produce the first of the heavy molecules (not included in the photochemistry). These molecules will irreversibly yield aerosol material. Meanwhile, the growth of these macromolecules is a sink for gas phase molecules included in the photochemistry (e.g., C_2H_2, HCN, HC_3N).

- During the initial steps of aerosol formation, the macromolecules grow from the first heavy molecules by including small gas phase molecules. Nucleation eventually occurs. Particles grow in mass and radius through several processes: chemical additions (chemical activity continues after nucleation), transition of gas phase macromolecules to the condensed phase, and coagulation. By the time the particles reach a radius of approximately 1–2 nm, microphysical considerations suggest that the further coagulation of particles occurs at constant mass, i.e., the addition of mass from the small gas phase molecules has become negligible. We define the precursor level as the transition between the regime where chemical addition of small molecules is significant and the regime where microphysical processes conserving the overall mass of aerosol material dominate. The source function used by microphysical models is the mass flux of aerosol material through this transition.
- This aerosol material, at the precursor level, is composed of macromolecules that have a certain mean length, i.e., that have incorporated, on average, a certain number of gas phase molecules during their chemical growth.

Based on these principles, we estimate the source function of precursors and their bulk elemental composition through these steps, using three sets of parameters:

- We propose three pathways for the initial reactions and the growth of macromolecules (polymers of C_2H_2 and HC_3N, polycyclic aromatics (PAHs) that may include HCN and HC_3N, and polymers of HCN and nitriles). These propositions are based on experimental results published by several teams (see Table I).
- The reaction rate coefficients (k, in $cm^3\ s^{-1}$) for these initial reactions are a first set of parameters.
- For each pathway, we propose gas phase molecules that may be incorporated in these macromolecules. The proportions of each molecule in the global macromolecule are controlled by a second set of parameters.
- The yield limiting the growth of a macromolecule (precursor level) is parameterized by the mean number of gas phase molecules incorporated in one macromolecule. We also refer to this parameter as the "length" of the polymers.
- The mass flux of aerosol material at the precursor level (i.e., the source function of the aerosols) is equal to the product between the mean molecular mass of macromolecules and the production rates of the first heavy molecules (initial reactions).

In laboratory experiments, tentative analogs to Titan's aerosols have been synthesized in order to obtain their properties. The study of these products has yielded some hints about the structure of the constituent macromolecules of the tholin particles, and in some cases the C/N and C/H ratios (Table I). How close tholins represent Titan's aerosols is in debate, but still, understanding the process which makes tholins can certainly help. Using these experiments, we have identified three possible pathways leading from parent molecules (C_2H_2, HCN, HC_3N and other nitriles, and C_6H_6) to macromolecules that will be the building blocks of the precursors. These pathways are described in Section 2. In Section 3, the parameterization of these pathways is detailed, and quantities of interest (mass production rates of the different channels, loss of the parent molecules, and C/N and C/H ratios) can be evaluated. This model is then applied to the atmosphere of Titan in Section 4.

2. INFORMATION FROM EXPERIMENTS

Numerous experiments have been done in order to synthesize tholins, analogs for Titan's aerosols. The conditions in the laboratories have been varied while trying to get as near to conditions in Titan's atmosphere as possible. Table I presents a summary of these experiments, with some results on the analysis of the products. Since the optical properties of tholins provide good matches to the properties of Titan's haze (Khare *et al.* 1984, Sagan *et al.* 1992), it is reasonable to assume that the production processes for tholins are close to those occurring in Titan's atmosphere. Most of the C/N ratios measured in the tholins are low (between 1.5 and 11), so we expect a fairly significant amount of nitrogen to be incorporated in the macromolecules during the chemical processes. We used the information provided by these experiments to identify several pathways from gas molecules to aerosol particles. Possible pathways we analyze in this paper include different kinds of polymers (C_2H_2, HC_3N, HCN), polyynes and cyanopolyynes, and aromatics (PAHs).

Polymers of C_2H_2 and HC_3N. These are obtained by polymerization of acetylene, or of a mixture of acetylene and cyanoacetylene. One possible structure for these polymers is described in Clarke and Ferris (1997). Clarke and Ferris (1997) also indicate the incorporation of other molecules in these polymers (CH_4, C_2H_6, and CO), but it seems to be of second order. This incorporation should also occur in the case of Titan's atmosphere, but we restrict our study to acetylene and cyanoacetylene only as a first approximation.

Polyaromatics. Polyaromatic compounds have been detected in laboratory tholins from the Khare *et al.* (1984) experiment (Sagan *et al.* 1993, Khare *et al.* 2001). Previous theoretical work has investigated the growth of the PAHs from benzene by addition of acetylene (Wang and Frenklach 1994, Wong *et al.* 2000, Bauschlicher and Ricca 2000). Nitrogen atoms could be incorporated in the cycles through the addition of HCN or HC_3N instead of acetylene (Ricca *et al.* 2001). Reaction rates and pathways for this growth are mostly studied at high temperatures (combustion), but some studies cover those as low as room temperature, which can allow a tentative extrapolation for Titan's atmospheric conditions (100–200 K).

Polymers of HCN. Coll *et al.* (1999) report that polymers of HCN could be part of the tholins they produced. In this

TABLE I
Experiments of Laboratory Synthesis of Titan's Aerosol Analogs

Papers	Energy source	T (K)	p (mb)	Initial gas mix	Gas[a]	Aerosol particles	C/N	C/H
Khare *et al.* 1984	Discharge	300	0.2	90% N_2, 10% CH_4	—	Tholins		
Sagan and Thompson 1984	Discharge	300	>10	90% N_2, 10% CH_4	—	Tholins	2	0.6
Bar-Nun *et al.* 1988	UV	300	270	Ar, 5% C_2H_2	—	polyC_2H_2		
				Ar, 5% C_2H_4	—	polyC_2H_4		
				Ar, 5% HCN	—	polyHCN		
Thompson *et al.* 1991	Cold plasma	300	17	90% N_2, 10% CH_4	X	Tholins		
			0.24					
Scatterwood *et al.* 1992	UV	300	73	N_2, 2% C_2H_2	—	polyC_2H_2		
				N_2, 2% C_2H_4	—	polyC_2H_4		
				He, 2% HCN	—	polyHCN		
				Mix	—	polyC_2H_2		
McDonald *et al.* 1994	Cold plasma	300	1	90% N_2, 10% CH_4	—	Tholins	1.5	0.6
Coll *et al.* 1995	Discharge	150	900	90% N_2, 10% CH_4	X	Tholins	11	1
McKay 1996	Discharge	300	1000	90% N_2, 10% CH_4	—	Tholins	5.5	1
Clarke and Ferris 1997	UV	300	330	90% C_2H_2, 10% HC_3N	—	polyC_2H_2/HC_3N	6.4	1.6
Coll *et al.* 1999	Cold plasma	150	2	98% N_2, 2% CH_4	X	Tholins (including polyHCN?)	2.8	0.8
Khare *et al.* 2001	Discharge	300	71	90% N_2, 10% CH_4	X	Tholins		

[a] An "X" in this column indicates that the composition of the resulting gas phase has been studied.

experiment, as well as in other similar experiments (Thompson *et al.* 1991, McDonald *et al.* 1994), nitrogen has to be incorporated in large quantities to get the observed low C/N ratio, and the obvious candidate is HCN, considering that it is the dominant N-bearing compound (other than N_2) in the gas phase. The question is, in these experiments, what exactly is produced? HCN could be incorporated as a copolymer in an aliphatic polymer, together with C_2H_2 and HC_3N (but we are unaware of any possible structure), or it could polymerize on its own. Matthews (1992) presents a study of these polymers, and Minard *et al.* (1998) discuss possible structures for their formation. Thompson and Sagan (1989) propose another possible structure for a more general polymerization of nitriles.

Polyynes and cyanopolyynes. The structure of these molecules is A-$(C{\equiv}C)_n$-B, with A and B being either H or CN. Many members of this group have been detected in the gaseous products (Coll *et al.* 1995, 1999). Only C_2H_2, HC_3N, and C_4H_2 have been observed in Titan's atmosphere. C_4N_2 has also been detected as a solid in the polar atmosphere of Titan. The C/N and C/H ratios in these compounds are high: the number of C atoms grows with the length of the molecule, while the number of H and/or N atoms is only 1 or 2. Their fate in Titan's atmosphere can be photolysis to smaller compounds, condensation in the low stratosphere, or incorporation in the aerosols. Since the C/N ratios available in the experiments are rather low (the largest is 11, in Coll *et al.* 1995) and the C/H ratios are all around 1, formation and incorporation of the polyynes and cyanopolyynes may not be a dominant growth mechanism for experimental tholins. Despite the differences between the pressures used in experiments and the pressures in the atmosphere of Titan (in the [200–600] km range in altitude), we assume here that these products are also of second order in the constitutive material of aerosol precursors.

Whether the products obtained in the experiments are long chains or aromatics, or a mix of both, is in debate. In this paper, we concentrate on the first three mechanisms: polymerization of a mixture of acetylene and cyanoacetylene (polymer 1), PAHs' growth from addition of acetylene on benzene rings (polymer 2, which could incorporate some HCN and HC_3N), and the polymerization of hydrogen cyanide and other nitriles (polymer 3). We assume that the tholins and Titan's aerosols are mainly a mixture of these types of macromolecules, to first order.

3. PARAMETERIZATION OF POLYMER FORMATION

In this section, we discuss the proposed mechanisms for polymer growth, and the necessary assumptions that we had to make. In each case a set of parameters is isolated. These are summarized in Table II. For each pathway, initial reactions are detailed. Their rate coefficients (k, in $cm^3\ s^{-1}$) are the first parameters. Once these reactions have occurred, the products are assumed to be incorporated ultimately into precursor particles. The parameters (α, β, γ) characterize the proportions of each small molecule incorporated in the global macromolecule. The macromolecules grow through addition of these small molecules until they reach the precursor level. These parameterizations allow us to calculate the mass production rates, the C/N and C/H ratios, and the incorporation rates of the parent molecules (C_2H_2, HCN, HC_3N, and other nitriles).

3.1. Acetylene Polymer (Polymer 1)

The exact structure of the polymers of acetylene, or of a mixture of acetylene and cyanoacetylene (Bar-Nun *et al.* 1988, Clarke and Ferris 1997), is not well known. It could be chains of double bonds C=C (as proposed by Clarke and Ferris (1997)), a family called vinylacetylenes (VA) in Dimitrov and Bar-Nun (1997), As a mechanism of their formation, one possibility is an attack on the triple bond in either acetylene or cyanoacetylene by a radical site at the end of the chain.

$$\textit{Growth scheme:}\quad R_n^{\cdot} + \begin{matrix} C_2H_2 \\ HC_3N \end{matrix} \xrightarrow[k_B=\alpha k_A]{k_A} R_{n+1}^{\cdot},$$

where $R_n^{\cdot}$ represents an intermediate step in the polymerization process. Its structure is shown in Fig. 1. This mechanism is reported as dominant for the growth of the VA family in the context of the model developed by Dimitrov and Bar-Nun (1997). The rates k_A and k_B are not known, but the main parameter we use is $\alpha = k_B/k_A$. It will determine the proportions of acetylene and cyanoacetylene incorporated in the polymer, and the initial reactions will yield the evaluation of the production rates. In this parameterization, the exact process of the polymerization is not crucial. Once the initial products are formed, we assume that they will ultimately form precursors with a mass determined by the incorporated gaseous molecules. Whether other species are incorporated in such polymers is considered here to be second order. Clarke and Ferris (1997) described the incorporation of methane, ethane, and carbon monoxide, and it may be possible that HCN also gets incorporated in those chains, but we leave this question open.

Initial reactions. The initialization of the polymerization is not a simple question. It could start with the radical C_4H_3 or its nitrile equivalent C_4H_2CN.

TABLE II
Proposed Parameters

Polymer		Parameters
1/Poly-C_2H_2/HC_3N	$k_1^{(7,9)}$	Initial reaction rate coefficients (mainly $C_2H_2 + C_4H_3$), in $cm^3\ s^{-1}$
	α	Ratio between HC_3N and C_2H_2 addition rates
	N_1	Mean number of molecules in a precursor macromolecule
2/PAHs	$k_2^{(1,2)}$	Initial reaction rate coefficients ($C_2H_2 + A_1'$), in $cm^3\ s^{-1}$
	β_1	Ratio between HCN and C_2H_2 addition rates
	β_2	Ratio between HC_3N and C_2H_2 addition rates
	N_2	Mean number of molecules incorporated at the precursor level
3/Poly-nitriles	$k_3^{(1)}$	Initial reaction rate coefficient (HCNH + HCN), in $cm^3\ s^{-1}$
	γ_j	Ratio between nitriles and HCN addition rates
	N_3	Mean number of nitrile molecules in a precursor macromolecule

Titan's atmosphere, as discussed in photochemical models (e.g., Lebonnois *et al.* 2001). The rate coefficient $k_1^{(6)}$ has been estimated in previous photochemical models, but improved data are also necessary. The other rate coefficients are not known. Rough estimates can be made using an analogy between compounds for $k_1^{(2)}$, $k_1^{(3)}$, $k_1^{(5)}$, $k_1^{(8)}$, and $k_1^{(9)}$.

Initial scheme (1a):

$$C_2H + C_2H_2 \xrightarrow{k_1^{(1)}} C_4H_2 + H \xrightarrow{k_1^{(4)}} C_4H_3 + H \xrightarrow{k_1^{(6)}} C_4H_4,\ C_4H_2 + H_2 \text{ or } 2C_2H_2.$$

$$C_4H_3 + (C_2H_2,\ HC_3N) \xrightarrow{k_1^{(7)}} \text{polymer 1 (e.g., l-}C_6H_5\text{)}.$$

Initial scheme (1b):

$$\begin{matrix} C_3N + C_2H_2 \\ \text{or} \\ C_2H + HC_3N \end{matrix} \xrightarrow[k_1^{(3)}]{k_1^{(2)}} HC_5N + H \xrightarrow{k_1^{(5)}} C_4H_2CN + H \xrightarrow{k_1^{(8)}} C_4H_3CN.$$

$$C_4H_2CN + (C_2H_2,\ HC_3N) \xrightarrow{k_1^{(9)}} \text{polymer 1}.$$

The reactions (C_4H_3, C_4H_2CN, l-C_6H_5) + (C_2H_2, HC_3N) → polymer 1 are the first step of the growth scheme.

Possible structures for C_4H_3 and l-C_6H_5 are shown in Fig. 1. C_3N is the nitrile equivalent of C_2H: $^{\cdot}C{\equiv}C{-}C{\equiv}N$, produced by the photodissociation of HC_3N. The reaction rate coefficients (in $cm^3\ s^{-1}$) $k_1^{(1)}$, $k_1^{(4)}$, and $k_1^{(7)}$ have been measured (see references in Table III), but these values may have significant uncertainties due to differing conditions between experimental works and

The parameter N_1 (where the subscript refers to the type of polymer) is the mean number of molecules that are incorporated in a chain at the precursor level (by definition, the added mass from gas phase to the aerosol material is negligible after this yield). The relative amounts of acetylene vs cyanoacetylene that are added depends on their respective addition rates and their

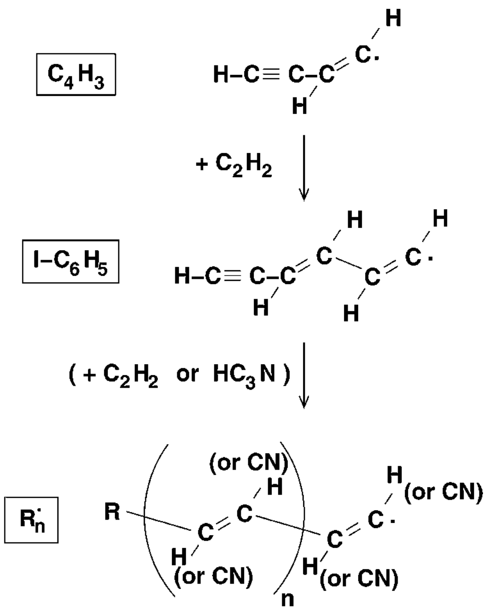

FIG. 1. Possible structures for compounds involved in polymer 1 formation.

respective number densities. The loss rate of acetylene to the formation of this polymer is

$$\frac{dn_{C_2H_2}}{dt} = \sum_{j=1}^{J} k_{j,C_2H_2} n_{R_j^{\cdot}} n_{C_2H_2} = A_{1,C_2H_2} n_{C_2H_2}, \tag{1}$$

where $R_j^{\cdot}$ ($j = 1$ to J) are all the different possible radicals that could react with acetylene during this polymer growth, and k_{j,C_2H_2} are the reaction rate coefficients associated with these reactions. The loss rate is therefore related to the acetylene concentration through

$$A_{1,C_2H_2} = \sum_{j=1}^{J} k_{j,C_2H_2} n_{R_j^{\cdot}}, \tag{2}$$

which we will call the "addition rate" of acetylene for the formation of polymer 1. A similar term is used for the various molecules and the various pathways all throughout this paper. The parameter α is defined as the ratio between cyanoacetylene and acetylene addition rates. Though this ratio depends in principle on the conditions in the gas under study, it may not vary much with these conditions if the ratio between the rate coefficient of the reaction $R_j^{\cdot} + HC_3N$ and the rate coefficient of the reaction $R_j^{\cdot} + C_2H_2$ does not depend significantly on the radical $R_j^{\cdot}$ and on the temperature and pressure of the gas (within a reasonable range). This hypothesis is plausible but certainly needs further investigation. The fractions of monomers corresponding to each molecule are

$$f_{1,C_2H_2} = \frac{n_{C_2H_2}}{n_{C_2H_2} + \alpha n_{HC_3N}}, \tag{3}$$

$$f_{1,HC_3N} = \frac{\alpha n_{HC_3N}}{n_{C_2H_2} + \alpha n_{HC_3N}}, \tag{4}$$

where n_i is the number density of the species i. The elemental ratios C/N and C/H can then be calculated. Using these fractions, we evaluate the mean numbers of C, H, and N atoms in the resulting polymer chain:

$$(C/N)_1 = \frac{2 f_{1,C_2H_2} + 3 f_{1,HC_3N}}{f_{1,HC_3N}}, \tag{5}$$

$$(C/H)_1 = \frac{2 f_{1,C_2H_2} + 3 f_{1,HC_3N}}{2 f_{1,C_2H_2} + f_{1,HC_3N}}. \tag{6}$$

The production rate of the polymers, p_1 (in cm^{-3} s^{-1}), can be evaluated as a function of the composition (concentrations of acetylene, cyanoacetylene, and other constituents included in the initialization scheme) and of the reaction rates of the initial reactions:

$$p_1 = n_{C_4H_3}\left(k_1^{(7a)} n_{C_2H_2} + k_1^{(7b)} n_{HC_3N}\right) + n_{C_4H_2CN}\left(k_1^{(9a)} n_{C_2H_2} + k_1^{(9b)} n_{HC_3N}\right). \tag{7}$$

Then the mass production rate, P_1 (in g cm^{-3} s^{-1}), is

$$P_1 = m_1 \times p_1, \tag{8}$$

where m_1 is the mean molecular mass of the polymer:

$$m_1 = N_1 \times \left(f_{1,C_2H_2} m_{C_2H_2} + f_{1,HC_3N} m_{HC_3N}\right). \tag{9}$$

The loss rates of acetylene and cyanoacetylene to the polymers are also calculated:

$$\left(\frac{dn_{C_2H_2}}{dt}\right)_1 = N_1 \times f_{1,C_2H_2} \times p_1, \tag{10}$$

$$\left(\frac{dn_{HC_3N}}{dt}\right)_1 = N_1 \times f_{1,HC_3N} \times p_1. \tag{11}$$

It should be noted that Eqs. (1) and (10) are two different expressions of the same variable: Eq. (1) is detailed from all the different reactions incorporating acetylene in the polymers; Eq. (10) is obtained because ($N_1 f_{1,C_2H_2}$) molecules of acetylene are statistically incorporated in each chain, and the initial production rate of the chains is p_1.

3.2. *PAH Growth (Polymer 2)*

If we consider a polymerization including aromatic compounds, the same formalism can be used. Polymerization can start through addition of acetylene on phenyl (noted A_1'), followed by another acetylene addition leading to A_2, $C_{10}H_8$ (Wang and Frenklach 1994, Wong *et al.* 2000, Bauschlicher and Ricca 2000). Addition would then continue and build up PAHs. The initial reaction considered in this pathway is:

$$A_1' + C_2H_2 \xrightarrow{k_2^{(1,2)}} \text{PAHs}.$$

HCN or HC_3N could also be added to form heterocycles (Ricca *et al.* 2001). The parameters we use are β_1 and β_2, where β_1 (respectively β_2) is the ratio between HCN (respectively HC_3N) and C_2H_2 addition rates. In the polymer 1, we use only two different possible monomers. Here, we have three different molecules that can be added to the growing macromolecule, and therefore two parameters (β_1, β_2) instead of one (α). Using the same formalism, the fractions of monomers included in the PAH corresponding to each molecule are:

$$f_{2,C_2H_2} = \frac{n_{C_2H_2}}{n_{C_2H_2} + \beta_1 n_{HCN} + \beta_2 n_{HC_3N}}, \quad (12)$$

$$f_{2,HCN} = \frac{\beta_1 n_{HCN}}{n_{C_2H_2} + \beta_1 n_{HCN} + \beta_2 n_{HC_3N}}, \quad (13)$$

$$f_{2,HC_3N} = \frac{\beta_2 n_{HC_3N}}{n_{C_2H_2} + \beta_1 n_{HCN} + \beta_2 n_{HC_3N}}. \quad (14)$$

The initial reactions determine the production rate p_2; then given a maximum size of growth (N_2 is the mean number of molecules included in the PAH at precursor level), the mass production rate P_2 can be calculated as

$$P_2 = m_2 \times p_2, \quad (15)$$

with

$$m_2 = N_2 \times \left(f_{2,C_2H_2} m_{C_2H_2} + f_{2,HCN} m_{HCN} + f_{2,HC_3N} m_{HC_3N}\right). \quad (16)$$

C/H is slightly over 1, depending on the size of the PAH, and C/N is

$$(C/N)_2 = \frac{2 f_{2,C_2H_2} + 3 f_{2,HC_3N} + f_{2,HCN}}{f_{2,HC_3N} + f_{2,HCN}}. \quad (17)$$

The loss rates of acetylene, hydrogen cyanide, and cyanoacetylene to this polymer are:

$$\left(\frac{dn_{C_2H_2}}{dt}\right)_2 = N_2 \times f_{2,C_2H_2} \times p_2, \quad (18)$$

$$\left(\frac{dn_{HCN}}{dt}\right)_2 = N_2 \times f_{2,HCN} \times p_2, \quad (19)$$

$$\left(\frac{dn_{HC_3N}}{dt}\right)_2 = N_2 \times f_{2,HC_3N} \times p_2. \quad (20)$$

3.3. HCN and Nitrile Polymer (Polymer 3)

The polymerization of HCN has been studied previously (Thompson and Sagan 1989, Matthews 1992, Minard *et al.* 1998). Despite the differences in the proposed structures, it seems possible to reconcile them, so we explore this possibility. Figure 2 presents the various reactions discussed here. Thompson and Sagan (1989) describe a formation scenario initiated by the reaction of an HCNH radical on a nitrile group. The polymer grows through subsequent N-terminus and C-radical interactions (reaction [b]). In Matthews (1992), scenarios for HCN polymerization proceed mainly by way of an HCN dimer

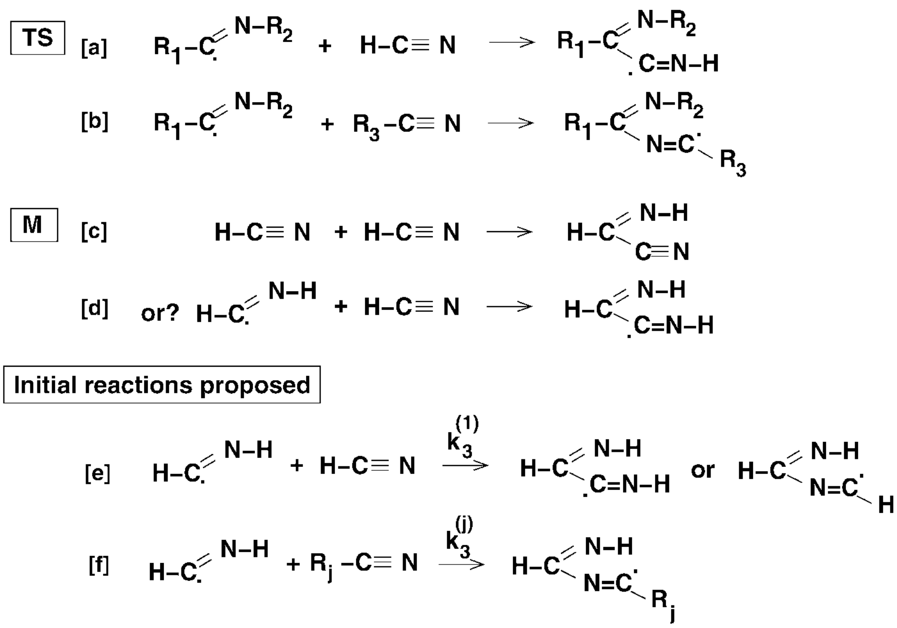

FIG. 2. Possible polymerization of nitriles (TS = Thompson and Sagan 1989; M = Matthews 1992).

(reaction [c]). Following the discussion of Thompson and Sagan (1989), it may be possible to reconcile the two schemes if the first HCN dimer were formed by reaction [d], involving the HCNH radical. This hypothesis remains to be addressed in more detail. The exact structure of HCN polymers remains difficult to assess, but based on these studies, we make the assumption that polymerization starts with the reactions between the HCNH radical and nitriles (reactions [e] and [f]). In Titan's atmosphere, the observed nitriles are HCN, then HC_3N, C_2N_2, and CH_3CN. In this study we add C_2H_3CN, which is predicted as a significant nitrile by our photochemical model of Titan's atmosphere (see Section 4) and has been detected as a significant nitrile in laboratory experiments (Coll *et al.* 1999). N_3 is the mean number of nitrile molecules in the precursors. Once again, the exact structure of the polymer is not crucial. The important factors are the initial reactions chosen and the relative reactivity of the various nitriles. For each nitrile R_jCN (R_j is C_2H, CN, CH_3, or C_2H_3), we define γ_j as the ratio of the addition rate of R_jCN to the addition rate of HCN.

The production rate of polymer 3, p_3 (cm^{-3} s^{-1}), can be evaluated as a function of the reaction rate coefficients of the inital reactions and the composition. The different proportions of each nitrile in the polymer are linked to the relative abundance of each nitrile, and its relative reactivity:

$$f_{3,\mathrm{HCN}} = \frac{n_{\mathrm{HCN}}}{n_{\mathrm{HCN}} + \sum_j \gamma_j n_{\mathrm{R}_j\mathrm{CN}}}, \tag{21}$$

$$f_{3,\mathrm{R}_j\mathrm{CN}} = \frac{\gamma_j n_{\mathrm{R}_j\mathrm{CN}}}{n_{\mathrm{HCN}} + \sum_j \gamma_j n_{\mathrm{R}_j\mathrm{CN}}}. \tag{22}$$

The mass production rate P_3 (g cm^{-3} s^{-1}) is then

$$P_3 = m_3 \times p_3, \tag{23}$$

with

$$m_3 = N_3 \times \left(f_{3,\mathrm{HCN}} m_{\mathrm{HCN}} + \sum_j f_{3,\mathrm{R}_j\mathrm{CN}} m_{\mathrm{R}_j\mathrm{CN}} \right). \tag{24}$$

The C/N and C/H ratios can be calculated, as well as the loss rates of the nitriles to the polymer,

$$(\mathrm{C/N})_3 = \frac{f_{3,\mathrm{HCN}} + \sum_j a_j^{\mathrm{C}} f_{3,\mathrm{R}_j\mathrm{CN}}}{f_{3,\mathrm{HCN}} + \sum_j a_j^{\mathrm{N}} f_{3,\mathrm{R}_j\mathrm{CN}}}, \tag{25}$$

$$(\mathrm{C/H})_3 = \frac{f_{3,\mathrm{HCN}} + \sum_j a_j^{\mathrm{C}} f_{3,\mathrm{R}_j\mathrm{CN}}}{f_{3,\mathrm{HCN}} + \sum_j a_j^{\mathrm{H}} f_{3,\mathrm{R}_j\mathrm{CN}}}, \tag{26}$$

where a_j^{C}, a_j^{N}, and a_j^{H} are the numbers of C, N, and H atoms (respectively) in the R_jCN molecule and

$$\left(\frac{dn_{\mathrm{R}_j\mathrm{CN}}}{dt} \right)_3 = N_3 \times f_{3,\mathrm{R}_j\mathrm{CN}} \times p_3. \tag{27}$$

3.4. *Mixing the Various Polymers*

The precursor level is defined as the yield where chemical growth through addition of mass from the gas phase becomes negligible. Chemical activity is still present (e.g., aging of the polymers; see Dimitrov and Bar-Nun (2002)), but the particles evolve at approximately constant mass, without absorbing any more gas molecules. This statement does not concern possible condensation of gas phase molecules on aerosol particles in the low stratosphere and troposphere (typically between 40 and 150 km altitude), which is a problem that is beyond the scope of this paper.

The total mass production rate of the haze is the sum of the different pathways, and the C/N and C/H mean ratios can be calculated:

$$\mathrm{C/N} = \frac{N_1 p_1 (2 f_{1,\mathrm{C_2H_2}} + 3 f_{1,\mathrm{HC_3N}}) + N_2 p_2 (2 f_{2,\mathrm{C_2H_2}} + 3 f_{2,\mathrm{HC_3N}} + f_{2,\mathrm{HCN}}) + N_3 p_3 (f_{3,\mathrm{HCN}} + \sum_j a_j^{\mathrm{C}} f_{3,\mathrm{R}_j\mathrm{CN}})}{N_1 p_1 f_{1,\mathrm{HC_3N}} + N_2 p_2 (f_{2,\mathrm{HC_3N}} + f_{2,\mathrm{HCN}}) + N_3 p_3 (f_{3,\mathrm{HCN}} + \sum_j a_j^{\mathrm{N}} f_{3,\mathrm{R}_j\mathrm{CN}})}, \tag{28}$$

$$\mathrm{C/H} = \frac{N_1 p_1 (2 f_{1,\mathrm{C_2H_2}} + 3 f_{1,\mathrm{HC_3N}}) + N_2 p_2 (2 f_{2,\mathrm{C_2H_2}} + 3 f_{2,\mathrm{HC_3N}} + f_{2,\mathrm{HCN}}) + N_3 p_3 (f_{3,\mathrm{HCN}} + \sum_j a_j^{\mathrm{C}} f_{3,\mathrm{R}_j\mathrm{CN}})}{N_1 p_1 (2 f_{1,\mathrm{C_2H_2}} + f_{1,\mathrm{HC_3N}}) + N_2 p_2 (2 f_{2,\mathrm{C_2H_2}} + f_{2,\mathrm{HC_3N}} + f_{2,\mathrm{HCN}}) + N_3 p_3 (f_{3,\mathrm{HCN}} + \sum_j a_j^{\mathrm{H}} f_{3,\mathrm{R}_j\mathrm{CN}})}. \tag{29}$$

3.5. *Discussion of Parameters*

Table II summarizes the parameters chosen for all polymers. The rate coefficients (measured or estimated) for the initial reactions of each scheme are given in Table III. These reaction rate coefficients have a significant uncertainty. The rate coefficient of HCNH on HCN ($k_3^{(1)}$) is not known. As a first assumption, we estimate its value from the reaction between C_2H_3 and HCN.

Ratios between addition rates. From a mixture of 250 Torr of acetylene and 25 Torr of cyanoacetylene, Clarke and Ferris (1997) measured a C/N ratio of 6.36, and a H/N ratio of 3.86. The polymer they report is our first pathway. Using Eqs. (5) and (6) and a C_2H_2/HC_3N concentration ratio equal to 10, the C/N and C/H ratios can be fairly well reproduced for $\alpha = 6$ (C/N = 6.33 and H/N = 4.33). This is consistent with laboratory studies showing cyanoacetylene to be two to five times more reactive than acetylene toward polymer formation (Clarke and Ferris 1995, 1997).

The studies by Ricca *et al.* (2001) can help constrain β_1 and β_2. The addition step for HCN or HC_3N in the process of ring formation shows a barrier very similar to the C_2H_2 addition step. The nitrogen atom will then induce a higher barrier in the ring closure process, but this will not have consequences on the f_2

TABLE III
Useful Reaction Rates

Reaction	Reaction rate coefficients ($cm^3\ s^{-1}$)	References
$C_2H_2 + C_2H \rightarrow C_4H_2 + H$	$k_1^{(1)} = 8.6 \times 10^{-16}\, T^{1.8} e^{474/T}$	Opansky and Leone 1996a
$C_2H_2 + C_3N \rightarrow HC_5N + H$	$k_1^{(2)} = 8.6 \times 10^{-16}\, T^{1.8} e^{474/T}$	Estimated from $k_1^{(1)a}$
$HC_3N + C_2H \rightarrow HC_5N + H$	$k_1^{(3)} = 8.6 \times 10^{-16}\, T^{1.8} e^{474/T}$	Estimated from $k_1^{(1)a}$
$C_4H_2 + H + M \rightarrow C_4H_3 + M$	$k_1^{(4)}$: $k_\infty = 1.39 \times 10^{-10}\, e^{-1184/T}$	Nava *et al.* 1986
	$k_0 = 1 \times 10^{-28\, b}$	Yung *et al.* 1984
$HC_5N + H \rightarrow C_4H_2CN$	$k_1^{(5)}$: $k_\infty = 1.39 \times 10^{-10} e^{-1184/T}$?	Estimated from $k_1^{(4)a}$
	$k_0 = 1 \times 10^{-28}?^{b}$	
$C_4H_3 + H \rightarrow C_4H_4$	$k_1^{(6a)} = 8.56 \times 10^{-10} e^{-405/T}$	Toublanc *et al.* 1995
$C_4H_3 + H \rightarrow C_4H_2 + H_2$	$k_1^{(6b)} = 1.2 \times 10^{-11}$	Yung *et al.* 1984
$C_4H_3 + H \rightarrow 2C_2H_2$	$k_1^{(6c)} = 3.3 \times 10^{-12}$	Yung *et al.* 1984
$C_4H_3 + C_2H_2 \rightarrow$ l-C_6H_5	$k_1^{(7a)} = 2 \times 10^{-16}$	Wang and Frenklach 1994
$C_4H_3 + HC_3N$ ($\rightarrow$ polymer 1)	$k_1^{(7b)} = 1.2 \times 10^{-15}$	Estimated from $\alpha \times k_1^{(7)}$
$C_4H_2CN + H \rightarrow C_4H_3CN$	$k_1^{(8)} = 8.56 \times 10^{-10} e^{-405/T}$?	Estimated from $k_1^{(6a)a}$
$C_4H_2CN + C_2H_2$ ($\rightarrow$ polymer 1)	$k_1^{(9a)} \sim 2 \times 10^{-16}$?	Estimated from $k_1^{(7)a}$
$C_4H_2CN + HC_3N$ ($\rightarrow$ polymer 1)	$k_1^{(9b)} \sim 1.2 \times 10^{-15}$?	Estimated from $\alpha \times k_1^{(7)a}$
l-$C_6H_5 + C_2H_2$ ($\rightarrow$ polymer 1)	2×10^{-16}?	Estimated from $k_1^{(7)c}$
l-$C_6H_5 + HC_3N$ ($\rightarrow$ polymer 1)	1.2×10^{-15}?	Estimated from $\alpha \times k_1^{(7)c}$
$A_1' + C_2H_2 \rightarrow A_1C_2H + H$	$k_2^{(1)} = 6.6 \times 10^{-17} T^{1.56} e^{-1913/T}$	Wang and Frenklach 1994
$A_1' + C_2H_2 \rightarrow A_1C_2H_2$	$k_2^{(2)} = 9.8 \times 10^{-13} T^{0.21} e^{-2517/T}$	Wang and Frenklach 1994
$HCNH + HCN$ ($\rightarrow$ polymer 3)	$k_3^{(1)} = 1 \times 10^{-12} e^{-900/T}$?	Estimated from $C_2H_3 + HCN$, Monks *et al.* 1993
$HCNH$ + nitriles ($\rightarrow$ polymer 3)	$k_3^{(j)} = \gamma_j \times k_3^{(1)}$	Parameters

[a] If we neglect the pathway through C_4H_2CN against the one through C_4H_3 (because of their relative abundance), then these values are secondary.
[b] k_0 values are in $cm^6\ s^{-1}$.
[c] We consider that once l-C_6H_5 is reached, all molecules will eventually yield a polymer. In this approximation, these rates are of secondary importance.

factors. It may slow the growth process, but it will eventually lead to precursor formation. As a rough hypothesis, we consider the assumption $\beta_1 \sim \beta_2 \sim 1$.

For polymer 3, in the absence of any data, we make the crude assumption that all nitriles have the same addition rate in the polymer. The parameters γ_j, ratios of the addition rate of a nitrile R_jCN to the addition rate of HCN, are therefore taken equal to 1 for all nitriles.

Length of the polymers. The mean length of the polymers (related to the N_i parameters) may be controlled by the details of the chain reactions. To estimate the extent of the molecules' incorporation at the precursor level (i.e., N_i), we use here a different approach. The usual density for aerosol particles is around 1 g cm^{-3} (Toon *et al.* 1992, Rannou *et al.* 1995). The size of the smallest particles used in these microphysical models for aerosol production is around 13 Å. The mass of these precursors is therefore on the order of 9×10^{-21} g, which corresponds to ~200 molecules of acetylene or hydrogen cyanide, or ~400 atoms of carbon and/or nitrogen. The precursor level used in our model is taken before or around that size. Therefore, we assume that N_i are all on the order of 10 to 100 gas molecules (and that $N_1 \sim N_2 \sim N_3$). Our chosen value is 20, which means that the precursors contain ~10 polymer macromolecules, which have each incorporated a mean value of 20 gas phase molecules before the chemical growth from the gas phase becomes negligible. This is consistent with the estimation given in Dimitrov and Bar-Nun (2002) stating that a particle of radius 3–8 Å may already consist of 12–20 macromolecules.

4. APPLICATION TO THE ATMOSPHERE OF TITAN

4.1. Model

In this study, we use a one-dimensional photochemical model, updated from Toublanc *et al.* (1995) (Lebonnois and Toublanc 1999, Lebonnois *et al.* 2001). The eddy diffusion coefficient profile has been modified in order to ensure that the vertical profiles of the atmospheric components obtained from this model are similar to those obtained with our recent two-dimensional model (Lebonnois *et al.* 2001). The vertical composition of the atmosphere is sensitive to the diffusion coefficient, but few constraints are available: the analyses of Voyager 1/IRIS observations by Coustenis *et al.* (1989) and Coustenis and Bézard

TABLE IV
Chosen Parameter Values

Parameter	Value
α	6
$\beta_1, \beta_2, \gamma_j$	1
N_1, N_2, N_3	20

(1995) constrain the composition in the 100–130-km region (low stratosphere), and a recent reanalysis of Voyager 1/UVS data by Vervack (1997) proposes vertical profiles for some compounds in the 500–800-km region. The two-dimensional dynamics we introduced in the stratosphere in our model (Lebonnois *et al.* 2001) have a major impact on these profiles in this region, yielding a more homogeneous stratosphere. The eddy diffusion coefficient profile has been tuned here to reproduce this effect and to bring most profiles in agreement with Voyager 1 observations (see Fig. 3). We have added to the model the production of aerosol precursors and the corresponding loss of gas phase components, using the parameterization described above. The chosen set of parameters is given in Table IV.

Our goals here are to get a first idea of the impact of this parameterization on the photochemical model, to evaluate the possible production rate (its vertical profile and its column integrated value) of precursors in these conditions, and to evaluate the composition we obtain for Titan's aerosol precursors.

4.2. Results

The profiles of components of interest for this study are shown in Fig. 3: hydrocarbon molecules (C_2H_2, C_4H_2, and benzene [A_1]), nitriles (HCN, HC_3N, C_2N_2, CH_3CN, and C_2H_3CN), and radicals (C_4H_3, HCNH, and phenyl [A_1']). The impact on their profiles of the loss of these molecules to the aerosols is also indicated in Fig. 3. As previously suggested by McKay (1996), this loss appears as a significant sink for the nitriles, but not for the hydrocarbons.

The profiles obtained for the mass production rates of each polymer are shown in Fig. 4. The maxima are all located between 150 and 200 km altitude. This is essentially a mirror of the density profiles of the various radicals, the maxima being slightly lowered by the increasing densities of acetylene and hydrogen cyanide. The column integrated values of the mass production rates are indicated in Table V, at two different steps: just after the initial reactions (before addition of any other gas molecules) and at the precursor level.

Polymers 1 and 3 are of similar importance, while the PAHs component (polymer 2) appears negligible by several orders of magnitude, due to the low mole fraction of phenyl (and therefore benzene) in the stratosphere and to the addition rate of acetylene on phenyl, which is much lower than the other initial reactions at this temperature (in the range 150–200 K).

The profiles of the C/N ratios are plotted in Fig. 5. This model (through Eq. (28)) gives a value of C/N in Titan's stratosphere of

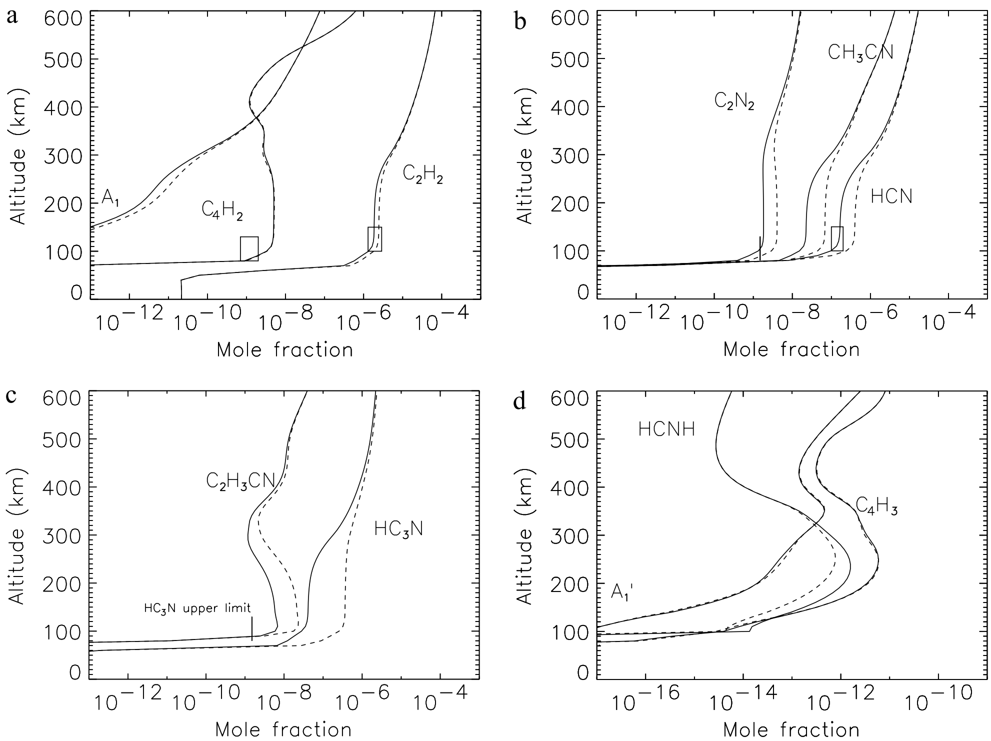

FIG. 3. Profiles of some compounds of interest: (a) hydrocarbons; (b, c) nitriles; (d) radicals. Solid lines: with the loss of these molecules to the haze; dashed lines: without this loss. The analysis of Voyager 1/IRIS spectra (Coustenis and Bézard 1995) is indicated as boxes (or vertical bars for upper limits).

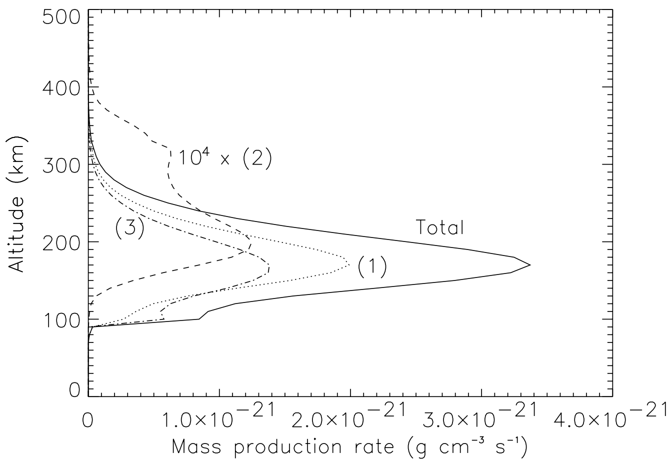

FIG. 4. Profiles of the mass production rates for each polymerization pathway.

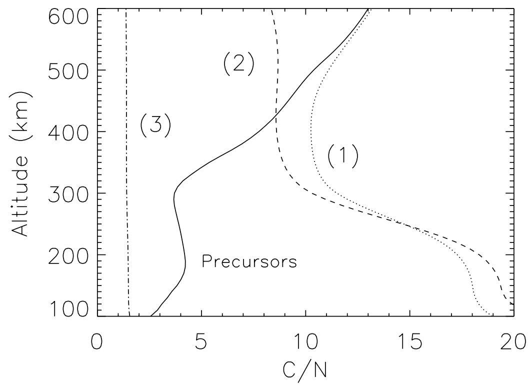

FIG. 5. C/N ratios for the various pathways and for the precursors.

approximately 4, which is a mix of polymer 1 with $(C/N)_1 \simeq 18$, and polymer 3 with $(C/N)_3 \simeq 1.5$. The C/H ratios are always slightly above 1.

4.3. Discussion

Experiments. Thompson *et al.* (1991), McDonald *et al.* (1994), and Coll *et al.* (1999) have produced tholins in experiments where gas phase compositions were close to Titan's stratosphere. Though the other experimental conditions (temperature, pressure, and energy source) are not a perfect reproduction of Titan's atmospheric conditions, the optical properties of tholins they produced provide good matches to the properties of Titan's haze (Sagan *et al*. 1992). The C/N ratios they measured (Table I) appear to be close to the global ratio we obtain around the maximum of the production. The C/H ratios they report are lower than unity, which is different from our value, but this can be understood as a consequence of the hydrogenation of the different C–C or C–N multiple bonds which can occur during the polymerization process and is not taken into account in our parameterization. Another process could also be the addition of methyl groups, due to the high abundance of methane.

TABLE V
Column Integrated Production Rate at Two Different Steps and the Altitude of the Maximum Production Rate z_{max}

	Initial reactions ($g\ cm^{-2}\ s^{-1}$)	Precursor level ($\mathcal{P}$) ($g\ cm^{-2}\ s^{-1}$)	z_{max} (km)
Polymer 1	2.8×10^{-15}	2.3×10^{-14}	150–200
Polymer 2	3.9×10^{-19}	2.4×10^{-18}	180–220
Polymer 3	2.5×10^{-15}	1.8×10^{-14}	150–200
Total	5.3×10^{-15}	4.1×10^{-14}	150–200
Toon *et al.* 1992	—	1.2×10^{-14}	200–300
Rannou *et al.* 1995	—	2.1×10^{-14}	385

In the Coll *et al.* (1999) experiment, HCN polymers (polymer 3) were reported likely to be present, and the C/N ratio is fairly similar to the one we get for our simulations, though slightly lower. For the series of experiments initiated by Khare *et al.* (1984), the presence of polyaromatics has been reported, though Thompson *et al.* (1991) do not indicate any production yield for benzene. It is worth noting that these experiments have been conducted at room temperature (300 K, compared to approximately 170 K in Titan's stratosphere and 100–150 K in Coll *et al.*'s (1999) experiment). This has a large impact on the addition rate of acetylene on the phenyl radical ($k_2^{(1+2)}$ varies by more than three orders of magnitude between 150 and 300 K), which could yield a much higher production rate of PAHs at room temperature, comparable to the two other kinds of polymers. Another possibility is that we are missing some other pathways to produce benzene (or other ring molecules), such as the reaction proposed in Arrington *et al.* (1998) between 1,3-butadiene and metastable diacetylene.

Microphysical models. Two different classes of microphysical models for the haze structure and evolution have been proposed to reproduce several sets of observational data (Titan's albedo, polarization of scattered light, and high phase angle brightness). The models differ in the shape of the aerosol particles. In one class the particles keep a spherical shape during their growth. In the other the particles form aggregates of small spheres, with a fractal shape. The maxima of production and the values of total mass production rates needed by the Toon *et al.* (1992) (spherical particles) and Rannou *et al.* (1995) (fractal particles) models are indicated in Table V, for comparison with our model.

The region of maximum mass production we obtain appears to be lower than expected by both these microphysical models. In our model, the position of this region is controlled by the vertical profiles of the radicals involved in the initial reactions (C_4H_3, HCNH). However, dynamical conditions in the stratosphere play an important role in the aerosols' evolution and distribution, and in the compounds' distribution. Winds associated with the general circulation are likely to carry small particles upward and may therefore result in a higher effective altitude of production than predicted here. This has been observed in coupled dynamics and microphysical models (Rannou *et al.*, submitted).

From methane photodissociation yields, Podolak and Bar-Nun (1979) estimated the production rate of C_2H_2 and C_2H_4 (which is then mostly photodissociated into acetylene). Comparing this value (3×10^{-14} g cm^{-2} s^{-1}) to our production rate for polymer 1 is not straightforward since this polymer contains HC_3N and since the photochemical model takes into account all the other sinks of acetylene and ethylene. But to first order, our value is indeed consistent with those simple photochemical considerations.

The total integrated mass production rate is higher than expected by both microphysical models, but the values we obtain at the precursor level should be taken as upper limits, since some intermediate molecules could be lost through condensation before they reach this level. Also, the influence of two-dimensional dynamics may affect the calculated production rate, as well as the values expected from the microphysical models.

To evaluate the role of the dynamical conditions in the stratosphere, it will be necessary to test this parameterization in a coupled model, including a general circulation model, a photochemical model, and a microphysical model, in order to draw a more complete conclusion.

Variations of parameters. In order to test the sensitivity of our results against parameter variations, we varied the values of N_i, α, β_1, β_2, γ_j, and $k_3^{(1)}$. First, we looked at the impact of the lengths of the chains at the precursor level (N_i) on the production rates of the three kinds of polymers. Were the composition of the gas phase fixed, the mass production rate P_i would be proportional to N_i (Eqs. (8) and (9) for pathway 1) in the context of this model. This only means that for a given production rate of the first heavy molecules, the more parent molecules are incorporated in a polymer, the heavier the macromolecules that constitute precursors and the higher the total mass production rate of precursors. But increasing N_i can affect the vertical profiles of gas phase molecules, if this loss to the haze becomes a dominant sink. Simulations were done with $N_i = 20, 50$, and 80. The integrated mass production rates $\mathcal{P}_i$ as functions of N_i are plotted in Fig. 6. $\mathcal{P}_1$ and $\mathcal{P}_2$ vary significantly with N_1 and N_2, respectively, because this sink is not dominant for the hydrocarbons, and therefore p_1 and p_2 only vary slightly with N_1 and N_2. This is not the case for $\mathcal{P}_3$, because this sink is significant for the nitriles. When N_3 increases, the nitrile mole fraction in the stratosphere decreases, and $\mathcal{P}_3$ reaches a limit.

The parameters α, β, and γ may be dependent on the conditions in the atmosphere of Titan (or in the laboratory experiments). Therefore, we modified them alternatively, raising or lowering their values by an order of magnitude. Concerning the first pathway, the value of α has an influence on the loss rate of HC_3N to the haze. Variation around $\alpha = 6$ does not affect C_2H_2 in the gas phase but has an impact on HC_3N stratospheric abundance, since this pathway represents a significant loss for this compound. It also affects the $(C/N)_1$ ratio (from ~10 to ~150),

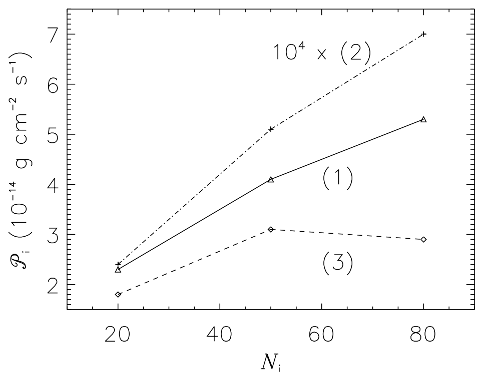

FIG. 6. Integrated mass production rate ($\mathcal{P}_i$, in g cm^{-2} s^{-1}) as a function of the parent molecules incorporated in the polymers at the precursor level (N_i).

as well as the mean molecular mass m_1 (small variations, around 5%), but the impact on the global C/N ratio and on the total mass production rate is small in the stratosphere (within 10%). Because polymer 2 is negligible compared to polymer 3, the values of β_1 and β_2 do not have any influence on the HCN and HC_3N vertical profiles. They also have little influence on m_2 and P_2: in the case of β_1, C_2H_2 and HCN have similar molecular mass, and in the case of β_2, the HC_3N mole fraction is significantly lower than both other compounds. The effect of β_1 and β_2 variations is only visible in the $(C/N)_2$ ratio, but due to its negligible production rate, this does not influence the global C/N ratio. We tested the impact of γ variations for HC_3N in a similar manner. When γ is raised for this nitrile, it increases its proportion in polymer 3. The molecular mass of the polymer changes accordingly (e.g., for HC_3N, it raises the molecular mass), affecting the mass production rate P_3. The $(C/N)_3$ is also slightly affected. The destruction rate of this nitrile increases, which affects its vertical profile. The overall variations of the global C/N ratio and mass production rate are small, within 30%.

Finally, variations on the value of the reaction rate coefficient between HCNH and HCN ($k_3^{(1)}$) induce correlated variations on the HCNH mole fraction profile (with only small variations on the nitriles' profiles), but the production rate remains largely unchanged. This is consistent with these reactions being the dominant sink of the HCNH radical in this model.

5. CONCLUSIONS

Based on experimental data, three pathways have been proposed in order to bridge the gap between the usual photochemical scheme and the microphysical models: polymers of acetylene and cyanoacetylene, polycyclic aromatic hydrocarbons (that could include some nitrogen in the rings), and polymers of HCN and other nitriles. The parameterization proposed here allows us to estimate mass production rates, loss rates of gas phase molecules to the aerosols, and the C/N ratio obtained in the precursors for each production channel. A basic set of parameters is used to apply this model to Titan's atmosphere. The following conclusions can then be derived:

1. We have been able to parameterize the mass production function of aerosol precursors from the photochemistry, given a certain number of assumptions: initial reactions leading to different types of polymers; relative incorporation of different kinds of monomers in each polymer structure; incorporation of gas molecules until the macromolecules reach a given size (precursor level); no heterogenous nor ion chemistry considered.

2. Though the comparison of the resulting C/N ratio and of the main products to the experiments is promising, the values determined for the mass production rate and the altitude of the peak production are only marginally in agreement with the values that one-dimensional microphysical models require.

3. Variations of the different parameters around their chosen values do not significantly affect the results, except for the length of the polymers at the precursor level.

4. This approach can help bridge the gap between gas phase molecules and the macromolecules that are building the aerosols in a simple way, without getting into the details of the polymer structures. Making this parameterization effective requires a qualitative understanding of the initial reactions, as well as a quantitative assessment of the various parameters. Efforts should continue in this direction, in particular through more detailed analysis of experimental data. The simultaneous characterization of the tholins (types of bonds, aliphatics vs PAHs, HCN polymers, and C/N and C/H ratios) and measurement of the gas phase composition (mole fractions of as many compounds as possible) are needed to help constrain the production mechanism of the tholins. It would be useful to have such experimental data for different initial conditions, especially with different initial mixtures: apart from the usual N_2/CH_4, it could also be C_2H_2/HCN (14/1), for example.

5. The first results we obtain here should also be tested with a coupled model (dynamics, photochemistry, and haze microphysics), especially since dynamics can significantly affect the required production conditions. This will help build a complete model of Titan's atmospheric system, as a powerful tool for the exploitation of Cassini/Huygens data.

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