

Titan's atmospheric haze: the case for HCN incorporation

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Abstract. It is suggested that the incorporation of HCN in Titan's atmospheric haze may be an important process affecting the HCN profile and the C/N ratio in Titan's haze. By introducing a loss to the haze term for HCN (i.e. a production term of "poly-HCN") in the photochemical model of Lara et al. (1996), we have improved the model's ability to simultaneously reproduce the observed HCN and C₂ hydrocarbon profiles in Titan's lower stratosphere. The loss rate of HCN by this process may be a few times 10⁸ cm⁻² s⁻¹. The calculated C/N ratio in the haze, assuming that the haze is primarily produced from C₆H₂, C₈H₂ and "poly-HCN", is approximately equal to 2, in agreement with the composition of laboratory tholin analogues.

Key words: molecular processes – planets and satellites: individual: Titan

1. Introduction

Lara et al. 1996 recently developed a detailed photochemical model of Titan's atmosphere, in which, in particular, they investigated the sensitivity of the calculated mixing ratio profiles to the atmospheric eddy diffusion coefficient (K). One of the important results of their model was that it appears difficult to simultaneously reproduce the observed mixing ratios of the major (C₂) hydrocarbons in the lower stratosphere and the observed HCN vertical distribution with a single eddy K profile. Specifically, in their model, fitting the HCN mixing profile at 100–300 km required a K profile in this altitude range 5–20 times larger than that necessary for the hydrocarbons.

In all the published Titan photochemical models (Yung et al. 1984; Toubanc et al. 1995; Lara et al. 1996), the main ultimate sink of light hydrocarbons (C₂, C₃, C₄) and nitriles is condensation. Hydrocarbon polymerization and formation of long-chain hydrocarbons also certainly takes place in Titan's atmosphere. However, because the models can handle only a limited number of compounds, and whose chemistry must be reasonably well known, the fate of heavy hydrocarbons (5 carbon atoms or more) is not followed in the models. For these involatile heavy species, condensation is no longer an effective sink, and their most likely

fate is transformation into organic material – tholins. Thus, the production rate of these unfollowed compounds – sometimes termed as "soot" (e.g. Toubanc et al. 1995) – provides an estimate of Titan's haze production. In this manner, Yung et al. 1984 estimated an integrated production rate of $\sim 10^8$ cm⁻² s⁻¹ for the heavy hydrocarbons (C₁₀ and above), equivalent to a haze production rate of about 2×10^{-14} g cm⁻² s⁻¹. The similarity with the values derived from microphysical models of the haze (about 10^{-14} g cm⁻² s⁻¹; McKay et al. 1989; Toon et al. 1992, Rannou et al. 1995) suggests that this approach, which effectively short-circuits unknown chemistry, is valid. Similarly, Lara et al. 1996 used the integrated production rate of C₆H₂ and C₈H₂ (unfollowed in their model) as an estimate of the haze production.

The loss of hydrocarbon to haze formation corresponds to a loss of about 4×10^8 C atoms cm⁻² s⁻¹ (McKay, 1996). Given the C production rate from the CH₄ photolysis (about 1×10^{10} cm⁻² s⁻¹), this is a minor sink for C. The same is not true for N, although, ironically, none of the preceding models has included the loss of N-bearing species to the solid phase. Laboratory simulations (see details below) indicate that the C/N ratio in the haze is of the order of 4 (within maybe a factor of 3). Thus, the N loss to the haze may be of the order of 10⁸ N atoms cm⁻² s⁻¹, i.e. typically 10% of the N production from N₂ dissociation. As stressed by McKay 1996, this is large enough that it must be considered by photochemical models.

The purpose of this paper is to present photochemical calculations of the HCN profile in Titan's atmosphere in the presence of a significant loss of N to the haze. We first improve the treatment of the dissociation of molecular nitrogen in Titan's atmosphere. We then show that including a sink of HCN to the haze can help to resolve the inability of the model to simultaneously reproduce the observed HCN and C₂ hydrocarbon abundances. The C/N ratio in the haze computed from the model is in satisfactory agreement with the most recent laboratory simulations.

2. Calculations

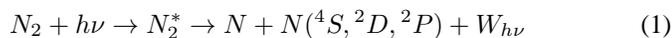
2.1. Atomic nitrogen production

We used the photochemical code developed by Lara et al. 1996. In this model, the N₂ molecule was considered as dissociated primarily by photolysis at UV wavelengths ($\lambda < 80$ nm), pro-

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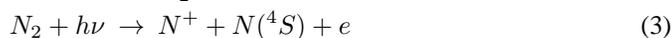
ducing two $N(^2D)$ atoms. (At low altitudes, N_2 dissociation due to galactic cosmic ray impact was also considered). This treatment of the N_2 UV photolysis, also used in the earlier model of Toublanc et al. (1995), is in fact incorrect, as below 80 nm ionization and dissociative ionization are the main channels of photon absorption. Direct photodissociation occurs only at 80–100 nm (Richards et al., 1981). Below 80 nm direct and dissociative photoionization of N_2 produces fast photoelectrons which in turn can dissociate N_2 .

The photochemical code of Lara et al. 1996 was modified to account for these various processes. The N_2 dissociation by UV photons occurs essentially as:

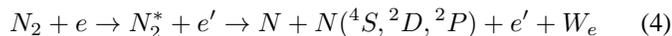


where $W_{h\nu}$ denotes excess kinetic energy. The relative branching ratios for $N(^4S):N(^2D):N(^2P)$ are about 50%: 30–40%: 10–20% (Zipf & McLaughlin 1978, Zipf et al. 1980). Since the $N(^2P)$ atoms are mainly deexcited into $N(^2D)$, the net effect is a production of approximately equal amounts of $N(^4S)$ and $N(^2D)$.

Direct and dissociative photoionization of N_2 below 80 nm can be written as:



The produced photoelectrons then dissociate N_2 as follows:



Laboratory studies indicate that discrete excited states (N_2^*) are formed, hence the dissociation of N_2 proceeds through the predissociation mechanism, mainly along the $N(^4S) + N(^2D)$ channel. We adopted partial dissociation cross sections and energy distributions of the dissociation fragments from the works of (Zipf & McLaughlin, 1978; Itikawa et al., 1986; Cosby, 1993).

Soft X-rays ($\lambda < 5$ nm) were also taken into account as a source of nitrogen atoms via more complex mechanisms involving photoelectrons and Auger-electrons (Gerard et al. 1997). The various paths of dissociation and dissociative ionization were included in the model using experimental data of Gardner & Samson, 1975 and Van Zyl & Stephen, 1994.

Finally, galactic cosmic ray impact was considered as in Lara et al. (1996). This process plays a role only at low altitudes (~ 100 km).

Calculations of kinetic rates of dissociative fragments formation and of photoelectron impact were carried out using a stochastic algorithm (Shematovich, 1987; Marov et al., 1997), in which all elementary photolytic steps are statistically modeled. The recommended EUVAC model for aeronomic applications (Richards et al. 1995) was used.

It must be noted that many of the reactions outlined above (reactions (2), (3), and all reactions involving X-rays) produce nitrogen ions (N^+ , N_2^+ , N_2^{++}). The fate of these ions cannot be tracked in our model which does not include ion-molecule reactions. Nonetheless these processes were considered because

they appear to represent sources of $N(^4S)$ and $N(^2D)$. The production rates of these “unfollowed” ions were calculated in order to check mass balance for elemental nitrogen. On the other hand, we cannot account for the influence of nitrogen ions on the HCN profile. Indeed, ionospheric models of Titan's atmosphere (Ip 1990, Keller et al. 1992) rely on a given atmospheric model based on photochemical calculations and assume that the neutral atmosphere is unchanged by the ionospheric reactions. In Titan's ionosphere, N^+ primarily reacts with CH_4 , producing mostly CH_3^+ and H_2CN^+ . CH_3^+ further reacts with CH_4 , producing heavy ions $C_xH_y^+$, which along with H_2CN^+ must be the dominant ions. Similarly N_2^+ reacts with CH_4 to produce CH_3^+ . H_2CN^+ recombines to H_2CN . As HCN is produced from $H_2CN + H$ and $H_2CN + N$, the ionospheric reactions may in fact increase the HCN production. In the absence of any coupled photochemical-ionospheric model (although Banaszekiewicz et al. (1998) have presented preliminary efforts in that direction), the importance of this process cannot be assessed. In any case, we argue below that even in the absence of ion-molecule reactions, a loss of HCN to the solid phase is required to fit the observed HCN profile. It can be predicted that this need would only be exacerbated if ion-molecule reactions were taken into account.

In Fig. 1, we show production rates for $N(^2D)$ and $N(^4S)$. More precisely, we separately show the production rates due to dissociation at 80–100 nm (“UV”). We also display the “total EUV” rates, which include the dissociative ionization from EUV and soft-X rays. Finally we show the rates due to photoelectrons and to galactic cosmic rays impact. At 1000 km and below, where only EUV and soft-X-ray radiation penetrates, the N_2 dissociation occurs mainly through photoelectron impact, with high energy photoelectrons and Auger-electrons causing cascade dissociation and ionization of molecular nitrogen. The $N(^2D)$ and $N(^4S)$ total production rates are very similar at all altitudes, although the partial contributions from solar radiation and photoelectrons are somewhat different.

The net dissociation rate of N_2 (integrated over altitude, and referenced to the tropopause) is $2.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ if only the direct UV photolysis at 80–100 nm is considered, and $5.7 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ if all processes are included. The latter number is (mostly by accident) essentially identical to what found by Lara et al. (1996), therefore, their results on the nitrogen compounds must remain essentially unchanged despite their erroneous approach of the N_2 dissociation. In particular, the problem outlined in the Introduction, namely the difficulty of reproducing the hydrocarbons and the vertical profile of HCN with a single eddy K profile, remains. This leads us to postulate that there exists an additional loss of N into the solid phase, which has not been included so far in photochemical models.

Besides this major improvement in the treatment of the N_2 dissociation, the Lara et al. (1996) code was modified to account for a recent measurement of the $C_2H + HCN \rightarrow HC_3N + H$ reaction rate (Hoobler & Leone 1997). Indeed, as noted by Hoobler & Leone, Lara et al. used a value ($1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) that is approximately 30 times larger than the value measured at room temperature. As we show below, this significantly affects

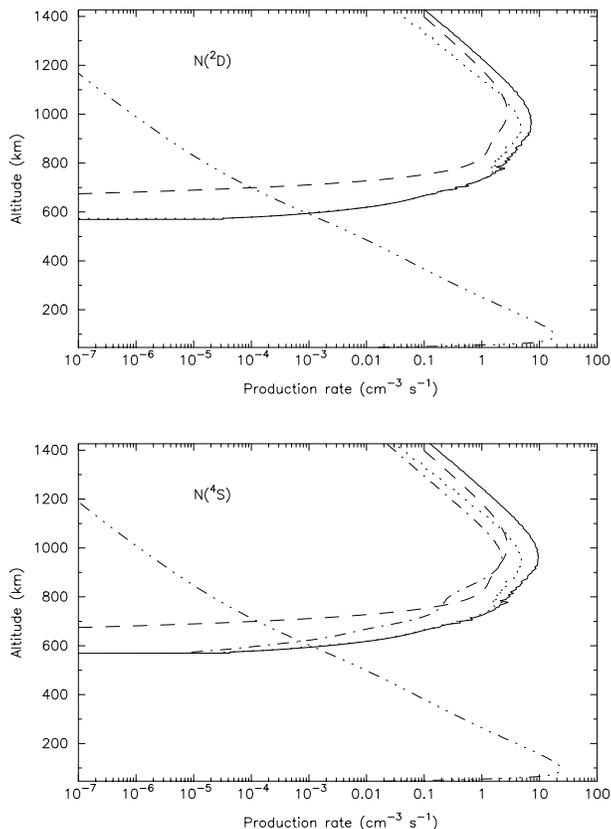


Fig. 1. Production rate ($\text{cm}^{-3} \text{s}^{-1}$) of $\text{N}(^4\text{S})$ and $\text{N}(^2\text{D})$ from N_2 dissociation. Dashed line: UV radiation between 80 and 100 nm. Dash-dotted line: EUV+soft-X-rays radiation between 1.1 and 80 nm. Dotted line: photoelectrons. Solid line: total by UV+EUV+soft-X-rays+photoelectrons. Dash-three dots line: GCR impact.

the calculated HC_3N production rate and vertical profile, but not so much the HCN profile, as this reaction is only a minor sink for HCN. (Hoobler & Leone further noted that, for the other major reaction producing HC_3N , namely $\text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H}$, Lara et al. (1996) quoted a reaction rate almost two orders of magnitude too high. This however comes from a typo in the expression of k_{102} in Table 2 of Lara et al., while the correct expression, $k_{102} = \min [4 \times 10^{-10}, 5.67 \times 10^{-9} T^{-0.55} \exp(-4/T)]$ was indeed used in the code of Lara et al., following Yang et al. (1992) and Sims et al. (1993)).

2.2. N incorporation into the haze

To model the loss of N to the haze, we proceeded by analogy with the loss of carbon through formation of polyacetylenes. The formation of polyynes occurs through successive reactions between C_2H_2 , C_2H , C_4H_2 , C_4H , etc... where the radicals are produced from the photolysis of C_2H_2 and C_4H_2 , and C_4H_2 is produced from $\text{C}_2\text{H} + \text{C}_2\text{H}_2$. Thus, the chemistry of C_2H_2 controls the production of polyynes. We thus assumed that the loss of N to the haze occurs through a sequence of unknown reactions involving HCN in the first step. Therefore, this haze production term represents a sink for HCN. For simplicity, we call this pro-

cess “polymerization of HCN” and the product “poly-HCN”, although some caveats must be given with this terminology. First, the polymerization of HCN has been observed to occur in conditions that are not relevant to the atmosphere of Titan. Such conditions include (i) the presence of an aqueous solution (ii) the presence of an anhydrous solvent and an additional compound capable of creating CN^- ions (iii) the presence of a base such as ammonia. The pure HCN polymerization in the gas phase requires high HCN concentration and high background gas density, and is therefore probably at most a minor loss of HCN in Titan’s atmosphere. However, laboratory experiments by Mizutani et al. (1972, 1975), Bar-Nun & Podolak 1979, Bar-Nun et al. 1988 and Scattergood 1995 have demonstrated the polymerization of HCN upon UV irradiation through formation of the CN radical (“photopolymerization”). Admittedly, the adequacy of these experiments to reproduce the Titan conditions may be criticized (important differences include the room vs. cold temperatures, the limited time of irradiation and the wall effects in the experimental design). In addition, the pathways, kinetics and kinetically limiting steps of the polymerization process are not identified. Also, since in Titan’s atmosphere, irradiation occurs on a complex mixture of gases, the copolymerization of species such as C_2H_2 , C_2H_4 and HCN into particles of mixed composition seems more likely than the photopolymerization of pure HCN. Nevertheless, these experiments suggest that heavy organic molecules containing HCN functional groups might be produced on Titan. Therefore, our terminology “poly-HCN” includes the HCN heteropolymers (or oligomers) (see Khare et al. 1994) along with (and probably more than) the true polymeric $(\text{HCN})_n$.

We stress that there are other conceivable ways to incorporate nitrogen into the haze. In particular, atomic N or HCN molecules may stick onto the aerosols. However, in the absence of laboratory data, a detailed modelling of this process is not possible. In this situation, we investigated the effect of a loss of HCN to the solid phase without trying to specify the loss mechanism.

In order to describe the “poly-HCN” production rate, we used two approaches. In the first one, we considered that it can be effectively expressed as a power law of the HCN number density, i.e.

$$P_{\text{poly-HCN}} = k[\text{HCN}]^\alpha \text{cm}^{-3} \text{s}^{-1} = L(\text{HCN})/\alpha \quad (5)$$

where $L(\text{HCN})$ is the loss rate of HCN (or, equivalently, N) to the solid phase. This approach is justified as follows. In the Lara et al. (1996) model, the vertically integrated production rate of C_6H_2 is $6 \times 10^{-15} \text{g cm}^{-2} \text{s}^{-1}$, in agreement with observed haze production rates (McKay et al. (1989); Toon et al. (1992); Rannou et al. (1995)). The corresponding value for C_8H_2 is 5 times less. Therefore, the loss of carbon to the haze is represented primarily by the production rate of C_6H_2 . As illustrated in Fig. 2, the volumic production rate of C_6H_2 approximately follows a dependence vs. the C_2H_2 number density in the form of Eq. (5). Specifically, Fig. 2 shows that this production occurs mostly at

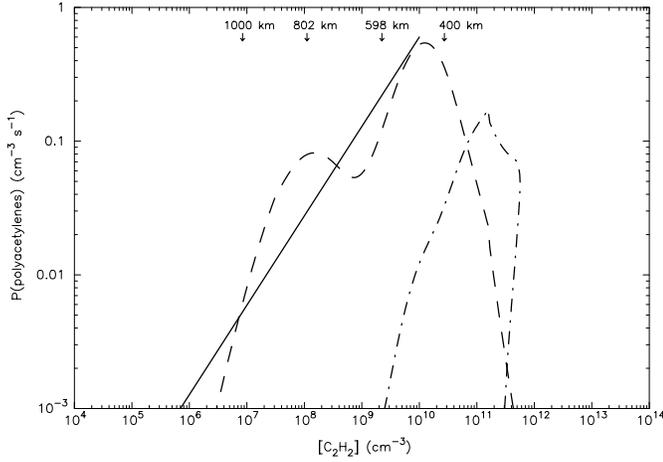


Fig. 2. Production rate ($\text{cm}^{-3} \text{s}^{-1}$) of polyacetylenes (C_6H_2 and C_8H_2) vs. C_2H_2 number density (cm^{-3}) in log scale. The solid line represents an approximate power-law fit of the $P_{\text{C}_6\text{H}_2}$ curve at altitudes higher than 400 km ($[\text{C}_2\text{H}_2] \leq 10^{10} \text{cm}^{-3}$) in the form $P_{\text{C}_6\text{H}_2} = 1.8 \times 10^{-13} [\text{C}_2\text{H}_2]^{1.5}$. The altitudes indicated by the vertical arrows pertain to the $P_{\text{C}_6\text{H}_2}$ curve.

levels where $[\text{C}_2\text{H}_2] \leq 1.0 \times 10^{10} \text{cm}^{-3}$, i.e. at altitudes higher than 400 km, and can be reasonably approximated by:

$$P_{\text{C}_6\text{H}_2} = 1.8 \times 10^{-13} [\text{C}_2\text{H}_2]^{1.5} \text{cm}^{-3} \text{s}^{-1} \quad (6)$$

For the HCN “polymerization”, we similarly took $\alpha = 1.5$ and varied the k coefficient in order to match to the observed vertical profile of HCN. Assuming similarity with C_2H_2 , which also undergoes photopolymerization, seems to be a reasonable starting point, but is admittedly speculative in the absence of a well-identified mechanism for the HCN polymerization.

In a second approach, we simply adopted a production rate in the form

$$P_{\text{poly-HCN}} = k' [\text{HCN}]^2 \text{cm}^{-3} \text{s}^{-1} \quad (7)$$

and similarly varied the value of k' . This is equivalent to assuming that the loss of N effectively proceeds through the polymerization reaction of HCN ($\text{HCN} + \text{HCN} \rightarrow \text{poly-HCN}$), which, as mentioned above, is not the most likely case. However, the main interest of testing another form for the loss to the haze is to demonstrate that the results are not overly sensitive to the details of the model. In both cases, the production of poly-HCN was limited to altitudes above 400 km.

The model with this additional loss term for HCN was run with the nominal eddy diffusion coefficient ($K(z)$) and the hydrocarbon distributions of Lara et al. 1996. This model allows a generally good fit of the observed hydrocarbon abundances in the Equatorial region.

3. Results and discussion

Model calculations with various values of k and k' are shown in Fig. 3 against several observational profiles of HCN. In this case, all processes leading to the production of $\text{N}(^4\text{S})$ and $\text{N}(^2\text{D})$ (as described above, UV, X-rays and photoelectrons) are accounted

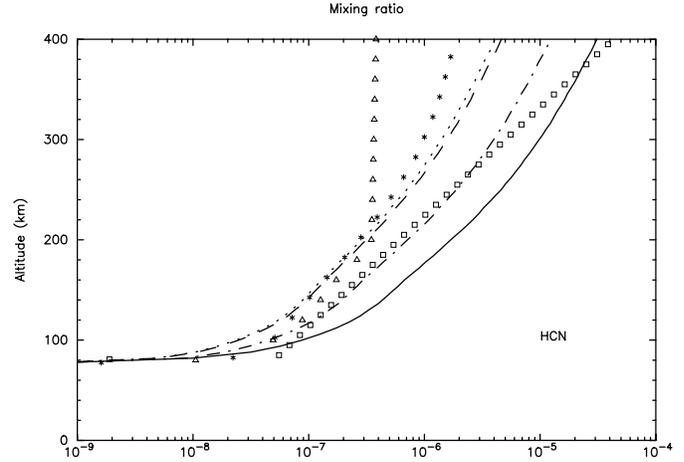


Fig. 3. Comparison between the observed HCN vertical profiles and the different model cases. In this case, the model includes all processes that dissociate N_2 : UV, EUV, soft X-rays, photoelectrons, GCR. Squares: Tanguy et al 1990. Triangles: Hidayat et al. 1997. Stars: Gurwell & Muhleman 1997. The observations are represented by symbols instead of lines for clarity, but the altitudes at which the symbols are plotted do not represent specific altitudes at which the measurements were made. Solid line: no HCN incorporation into the haze. Other lines include a loss rate to the haze in the form described in the text. Dash-dotted line: $k = 4 \times 10^{-14}$ and $\alpha = 1.5$. Dashed line: $k = 1.5 \times 10^{-13}$ and $\alpha = 1.5$. Dotted line: $k' = 3.2 \times 10^{-18}$ and $\alpha = 2$.

for. Consistent with Lara et al. 1996, we continue to find that, in the absence of an additional loss term for HCN, the model grossly overpredicts the HCN mixing ratio at 100–300 km. The fit is substantially improved by the inclusion of a loss to the haze term. The HCN distribution of Tanguy et al. 1990 can be satisfactorily reproduced with $P_{\text{poly-HCN}} = k [\text{HCN}]^{1.5}$ where $k = 4 \times 10^{-14}$. Similarly the HCN profile of Gurwell & Muhleman (1997) is reasonably well matched below 300 km with $k = 1.5 \times 10^{-13}$. Given the uncertainties on the measurements, we conclude that $k = 0.8 \times 10^{-13}$ within a factor of 2. A virtually identical fit of the Gurwell & Muhleman (1997) profile can be obtained with $P_{\text{poly-HCN}} = k' [\text{HCN}]^2$, where $k' = 3.2 \times 10^{-18}$. The fact that essentially identical fits can be obtained with the two different models means that it is not possible to infer something about a possible incorporation mechanism of HCN into the haze.

Also, with our choice of the eddy K profile, the models cannot reproduce the uniform HCN mixing ratio above 200 km found by Hidayat et al. 1997. A much larger K value is required there (Lara et al. 1996; Hidayat et al. 1997). We suggest that the measurements actually provide weak constraints on the HCN mixing ratio above 300 km.

In their model, Lara et al. 1996 were unable to reproduce the observed amount of HC_3N . Specifically, their baseline model overpredicted the HC_3N column density above 320 km by a factor about 300. As mentioned before, HC_3N is mostly produced from $\text{CN} + \text{C}_2\text{H}_2$ and $\text{HCN} + \text{C}_2\text{H}$. Therefore, the decrease of HCN associated with the loss of N to the solid phase, combined with the use of the lower reaction rate for $\text{HCN} + \text{C}_2\text{H}$

from Hoobler & Leone (1997), results in a decrease of the production rate of HC_3N . The overall effect of the HC_3N profile, however, is only a decrease of a factor of about 2. Therefore, the calculated HC_3N profile remains grossly unadequate. This problem may be associated with an incorrect handling of the HC_3N photolysis rate (see Lara et al. 1996).

The column loss of nitrogen to the haze is computed as being equal to α times the integrated production rate of the poly-HCN, where $\alpha=1.5$ and 2 for the two types of models respectively. The factor α comes from the fact that the production rate of each molecule of poly-HCN, as we have expressed it, represents the loss of α molecules of HCN. For $k = (0.4 - 1.5) \times 10^{-13}$ and $\alpha=1.5$, we obtain a loss rate of $(3.5-5.0) \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. Similarly, for the other model, $k' = 3.2 \times 10^{-18}$ and $\alpha=2$ lead to a loss rate of $5.1 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. With a nominal N_2 dissociation rate of $1.15 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ in our model, the loss of nitrogen to the haze represents 30–44% of the total loss of N. It is also 3–5 times larger than the HCN condensation rate. Thus we tend to confirm the basic premise of McKay 1996 that the production of tholin is an important sink for N and that it alters the HCN profile. We find that the effect is even more important than suggested by McKay 1996 who estimated that 12% of N is lost as solid organic material. We note however that this determination was based on the assumption of a C/N ratio of 4 in the haze. If this ratio is closer to 2, as suggested below, McKay's estimate would lead to about 25% loss of N to the haze, in reasonable agreement with our finding.

The C/N ratio in the haze can be calculated from the model, according to:

$$\frac{C}{N} = \frac{6 \int P_{\text{C}_6\text{H}_2} + 8 \int P_{\text{C}_8\text{H}_2} + \alpha \int P_{\text{poly-HCN}}}{\alpha \int P_{\text{poly-HCN}}} \quad (8)$$

where $\int P$ here represents integrated production rates. With respective productions rates of $4.8 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ and $9.2 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ for C_6H_2 and C_8H_2 respectively (Lara et al. 1996), we find $C/N = 1.7 - 2.0$. This value must be compared with findings from laboratory simulations. In an experiment where a $\text{CH}_4\text{-N}_2$ mixture with 10% CH_4 was submitted to a tesla discharge at a pressure ≥ 10 mbar, Sagan et al. 1984 found a C/N ratio of 1.93 (stoichiometry $\text{C}_8\text{H}_{13}\text{N}_4$). A very different result ($C/N=11$, stoichiometry $\text{C}_{11}\text{H}_{11}\text{N}$) was obtained by Coll et al. 1995. From a similar experiment, McKay et al. 1989 reported on an intermediate $C/N=5.5$ (stoichiometry $\text{C}_{11}\text{H}_{11}\text{N}_2$). Most recently, Coll et al. 1997a, 1997b described results from a more realistic simulator of Titan's atmosphere, important aspects of which are a continuous flow system, a cold plasma energy source, a low operating pressure (≤ 3 mbar), and the possibility to operate either at room or cold (≤ 200 K) temperatures. The measured value of the C/N ratio is 2.83 at room temperature (stoichiometry $\text{C}_6\text{H}_9\text{N}_2$) and 1.73 at low temperature. This compares remarkably well with our determination of 1.7–2.0 from fitting of the HCN profile. We note however that the laboratory measurements give a H/C ratio in the haze in the range 1–1.6. This is significantly larger than we infer ($H/C = 0.6-0.7$), since in our model the production of C_6H_2 (with

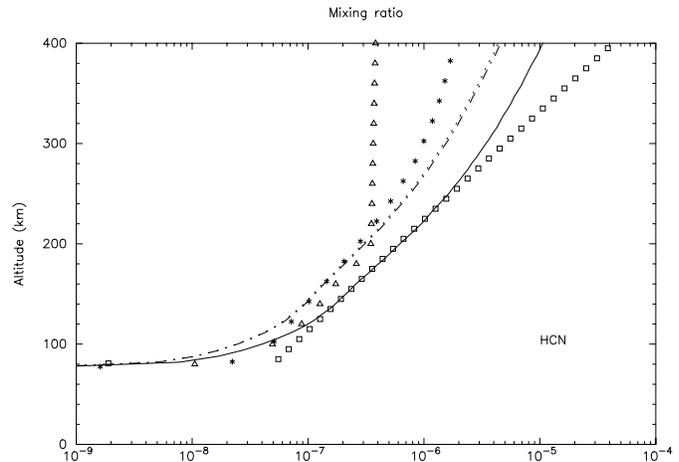


Fig. 4. Same as Fig. 3, but here the model includes only the dissociation of N_2 by solar UV at 80–100 nm and by GCR. Solid line: no HCN incorporation into the haze. Dashed line: $k = 6 \times 10^{-14}$ and $\alpha = 1.5$. Dotted line: $k' = 1.3 \times 10^{-18}$ and $\alpha = 2$.

a $H/C = 1/3$) and that of poly-HCN (with $H/C=1$) contribute approximately equally to the haze formation.

Toublanc et al. 1997 used a different approach to evaluate the importance of the HCN polymerization and the C/N ratio in the haze. Assuming, similar to our second case, a haze production rate for HCN polymerization in the form $P_{\text{poly-HCN}} = k'[\text{HCN}]^2$, they adjusted k' so that the total haze production rate (from polyynes and from poly-HCN) matched the observed value. From this, they inferred a C/N ratio in the haze of 1.4–3.6. This is in reasonable agreement with our findings.

While we regard the above model, including the secondary effect of photoelectrons, as the best description of the N_2 dissociation in Titan's atmosphere, we also investigated the effect of including only photolysis at 80–100nm as the source of $\text{N}(^4\text{S})$ and $\text{N}(^2\text{D})$ atoms. In this case, the N_2 dissociation rate is only $2.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. Including no loss to the haze allows an approximate fit to the Tanguy et al. 1990 HCN profile, but fitting the more recent profile of Gurwell et al. (1997) requires a loss term $P_{\text{poly-HCN}} = 6 \times 10^{-14}[\text{HCN}]^{1.5}$ or $P_{\text{poly-HCN}} = 1.3 \times 10^{-18}[\text{HCN}]^2$ (Fig. 4). This loss term is thus about 2.5 times less important than in the full model; the fraction of the nitrogen lost to the haze remains important at $\sim 23\%$.

In summary, we believe that McKay's 1996 suggestion that the loss to solid haze material is an important sink of nitrogen is reinforced by our calculations. We further suggest that (i) if the mechanism for such loss involves incorporation of HCN, through polymerization or any other process such as sticking, then it may help solving the conflict between the mixing profile of HCN and that of the C_2 hydrocarbons, and that (ii) the C/N in the haze as calculated from photochemistry is then consistent with the most recent laboratory simulations. We stress that our results should be regarded only as indicative of the importance of the process, as, in the absence of quantitative data (paths, rates...) on (co)polymerization rates of HCN in closely simulated Titan conditions, our approach and results cannot be more than approximate. We finally note that Clarke & Ferris 1997

have recently demonstrated in laboratory experiments the formation of HC_3N polymers and $\text{HC}_3\text{N}-\text{C}_2\text{H}_2$ copolymers upon irradiation; this process might also represent a significant sink of nitrogen to the Titan haze.

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References

- Banaszkiewicz M., L.-M. Lara, R. Rodrigo, Lopez-Moreno J.-J., Molina-Cuberos G., 1998, Nantes Symposium, 11–15 May 1998, p. 81
- Bar-Nun A., Podolak M., 1979, *Icarus* 38, 115–122
- Bar-Nun A., Kleinfeld I., Ganor E., 1988, *J. Geophys. Res.* 93, 8383–8387
- Clarke D.M., Ferris J.P., 1997, *Icarus* 127, 158–172
- Coll P., Coscia D., Gazeau M.C., et al., 1995, *Adv. Space Res.* 16, 93–103
- Coll P., Coscia D., Gazeau M.C., Raulin F., 1997a, *Ann. Geophys.* 19, 1113–1119
- Coll P., Coscia D., Gazeau M.C., Raulin F., 1997b, *Ann. Geophys.* 15, C775
- Cosby P.C., 1993, *J. Chem. Phys.* 98, 9544–9553
- Coustenis A., Bézard B., Gautier D., 1989, *Icarus* 80, 54–76
- Gardner J.L., Samson J.A.R., 1975, *J. Chem. Phys.* 62, 1447–1456
- Gerard J.C., Shematovich V.I., Bisikalo D.V., Duff J., 1997, *J. Geophys. Res.* 102, 285–294
- Gurwell M.A., Muhleman D.O., 1997, *Ann. Geophys.* 15, C778
- Hidayat T., Marten A., Bézard B., et al., 1997, *Icarus* 126, 170–182
- Hoobler R.J., Leone S.R., 1997, *J. Geophys. Res.* 102, E12, 28717–28723
- Ip W.-H., Titan's upper ionosphere, 1990, *Astrophys. J.* 362, 354–363
- Itikawa Y., Hayashi M., Ishimura A., et al., 1986, *J. Phys. Chem. Ref. Data* 15, 985–1010
- Keller C.N., Cravens T.E., Gan L., 1992, *J. Geophys. Res.* 97, 12117–12135
- Khare B.N., Sagan C., Thompson W.R., et al., 1994, *Can. J. Phys.* 72, 678–694
- Lara L.-M., Lellouch E., López-Moreno J.J., Rodrigo R., 1996, *J. Geophys. Res.* 101, 23261–23283
- Marov M.Ya., Shematovich I., Bisikalo D., Gerard J.-C., 1997, *Nonequilibrium processes in the planetary and cometary atmospheres: Theory and Applications.* Dordrecht: Kluwer Academic Publishers, 1–293
- McKay C.P., 1996, *Planet. Space Sci.* 44, 741–748
- McKay C.P., Pollack J.B., Courtin R., 1989, *Icarus* 80, 23–53
- Mizutani H., Mikuni H., Takahasi M., 1972, *Chem. Letters* 1972, 573–576
- Mizutani H., Mikuni H., Takahasi M., Noda H., 1975, *Origins of Life* 6, 513–525
- Rannou P., Cabane M., Chassefiere E., et al., 1995, *Icarus* 118, 355–372
- Richards P.G., Fennelly J.A., Torr D.G., 1994, *J. Geophys. Res.* 99, 8981–8990
- Richards P.G., Torr D.G., Torr M.R., 1981, *J. Geophys. Res.* 86, 1495–1498
- Sagan C., Khare B.N., Lewis J.S., 1984, *Organic matter in the Saturn system.* In: Gehrels T., Matthews M.S. (eds.) *Saturn.* Univ. Arizona Press, Tucson, pp 788–807
- Scattergood T.W., 1995, *Adv. Space Res.* 15, 313–316
- Shematovich V.I., 1987, *Numerical stochastic simulation of kinetics of atmospheric photochemistry.* In: Marov M. (ed.) *Mathematical problems of applied aeronomy.* Keldysh Inst. of Applied Math., Moscow, 199–209, (in Russian)
- Sims I.R., Queffelec J.L., Travers D., et al., *Chem. Phys. Lett.* 95, 211, 461–468
- Strobel D.F., Summers M.E., Xun Zhu, 1992, *Icarus* 100, 512–526
- Tanguy L.B., Bézard A., Marten D., et al., 1990, *Icarus* 85, 43–57
- Toon O.B., McKay C.P., Griffith C.A., Turco R.P., 1992, *Icarus* 95, 24–53
- Toublanc D., Parisot J.P., Brillet J., Gautier D., McKay C.P., 1995, *Icarus* 95, 24–53
- Toublanc D., Lilensten J., Galand M., McKay C.P., 1997, *Ann. Geophys.* 15, C786
- Van Zyl B., Stephen T.M., 1994, *Phys. Rev. A.* 50, 3164–3173
- Yang D.L., Lin M.C., Melius C.F., 1992, *J. Chem. Phys.* 97, 222–226
- Yung Y.L., Allen M., Pinto J., 1984, *Astrophys. J.* 55, 465–506
- Zipf E.C., McLaughlin R.W., 1978, *Planet. Space Sci.* 26, 449–462
- Zipf E.C., Espy P.S., Boyle C.F., 1980, *J. Geophys. Res.* 85, 687–696