

NOTE

An Update of Nitrile Photochemistry on Titan¹

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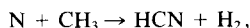
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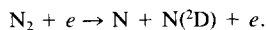
New chemical schemes leading to the formation of cyanogen (C₂N₂) and dicyanoacetylene (C₄N₂) in the upper atmosphere of Titan are proposed and examined in light of recent laboratory kinetics experiments and Voyager observations. © 1987

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Introduction. According to Yung *et al.* (1984), the primary source of nitrile compounds in the atmosphere of Titan is the reaction



where the nitrogen atoms are derived from electron impact dissociation of N₂,



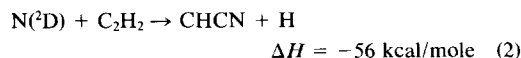
Cyanogen (C₂N₂) was thought to form via



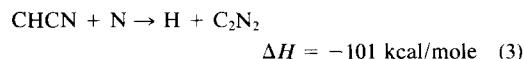
and the authors showed that this reaction could account for the observed abundance of C₂N₂ (Kunde *et al.* 1981) if the rate coefficient, k_1 , were as large as $3.1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. Recent experiments by Li *et al.* (1984) suggested that $k_1 = 1.8 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ at 300°K, which is considerably lower than the original estimate. So a new scheme has to be explored to explain the Voyager observations.

Recent laboratory spectroscopic studies strongly suggest that one of the unidentified emission features in the Voyager IRIS spectrum is due to C₄N₂ ice (Samuelson 1986, private communication). The chemistry of this molecule was not included in the model of Yung *et al.* (1984). In this note we examine a plausible mechanism for the formation of this species.

Some speculative chemistry. The reactions between nitrogen atoms in the ground state, N(⁴S), and hydrocarbons are now recognized to be slow (Michael 1980, Umemoto *et al.* 1986). The excited state, N(²D), should be more reactive. We propose a new reaction,



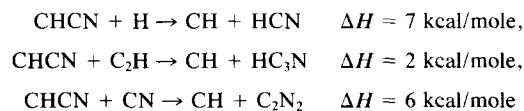
(unless otherwise stated, all enthalpies are taken from Safrany 1971). The most likely fate of CHCN is reaction with N atoms,



(Safrany and Jaster 1968), or disproportionation

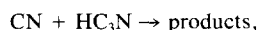


The latter reaction is based on analogy with the methylene radical disproportionation (Banyard *et al.* 1980, Laufer 1981). Other reactions such as

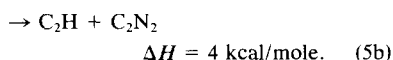
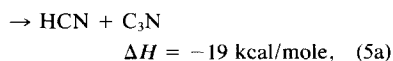
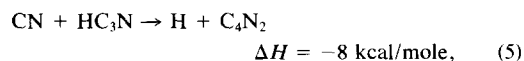


are endothermic and can be ignored.

There is another reaction which may also be important for producing C₄N₂ on Titan. A laboratory experiment studying the reaction between cyanoacetylene and the cyanide radical has recently been carried out by Okabe (1986, private communication). The rate coefficient for the overall reaction,



was determined to be about $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ at room temperature. The products are unknown. There are three possibilities,



Channel (5b) is slightly endothermic, and so it is

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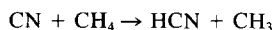
TABLE I

PARTIAL LIST OF CHEMICAL REACTIONS USED IN THE TITAN MODEL

	Reaction	Rate coefficient	Reference
R1	$\text{CN} + \text{HCN} \rightarrow \text{H} + \text{C}_2\text{N}_2$	1.8×10^{-14}	Li <i>et al.</i> 1984
R2	$\text{N}(^2\text{D}) + \text{C}_2\text{H}_2 \rightarrow \text{CHCN} + \text{H}$	1×10^{-11}	Estimated
R3	$\text{CHCN} + \text{N} \rightarrow \text{H} + \text{C}_2\text{N}_2$	1×10^{-12}	Estimated
R4	$2\text{CHCN} \rightarrow \text{H}_2 + \text{C}_4\text{N}_2$	5.0×10^{-11}	Estimate based on $\text{CH}_2 + \text{CH}_2$
R5	$\text{CN} + \text{HC}_3\text{N} \rightarrow \text{H} + \text{C}_4\text{N}_2$	1.0×10^{-11}	Estimate based on R6
R6	$\text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H}$	2.3×10^{-11}	Lichtin and Lin 1986
R7	$\text{C}_4\text{N}_2 + h\nu \rightarrow \text{C}_3\text{N} + \text{CN}$	1.6×10^{-7}	Connors <i>et al.</i> 1974; assume quantum yield of dissociation = 0.3
R8	$\text{C}_3\text{N} + \text{CH}_4 \rightarrow \text{HC}_3\text{N} + \text{CH}_3$	5×10^{-14}	Estimate based on $\text{CN} + \text{CH}_4$
R9	$\text{C}_3\text{N} + \text{C}_2\text{H}_6 \rightarrow \text{HC}_3\text{N} + \text{C}_2\text{H}_5$	1×10^{-11}	Estimate based on $\text{CN} + \text{C}_2\text{H}_6$
R10	$\text{N}(^2\text{D}) + \text{N}_2 \rightarrow \text{N} + \text{N}_2$	1.6×10^{-14}	Lin and Kaufman 1971

Note. All other reactions are the same as those given in Yung *et al.* (1984). The units for photodissociation and bimolecular reaction coefficients are sec^{-1} and $\text{cm}^3 \text{sec}^{-1}$, respectively.

unlikely to be the dominant pathway. Channel (5a) is an abstraction reaction. Experience tells us that an abstraction reaction such as



is relatively slow, with rate coefficient at room temper-

ature equal to $6 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ (Schacke *et al.* 1977). Since the C-H bond in HC_3N is stronger than the corresponding C-H bond in CH_4 , we expect $k_{5a} \sim 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$, a value that is much lower than Okabe's measurement for the overall rate coefficient. By elimination we conclude that channel (5), the

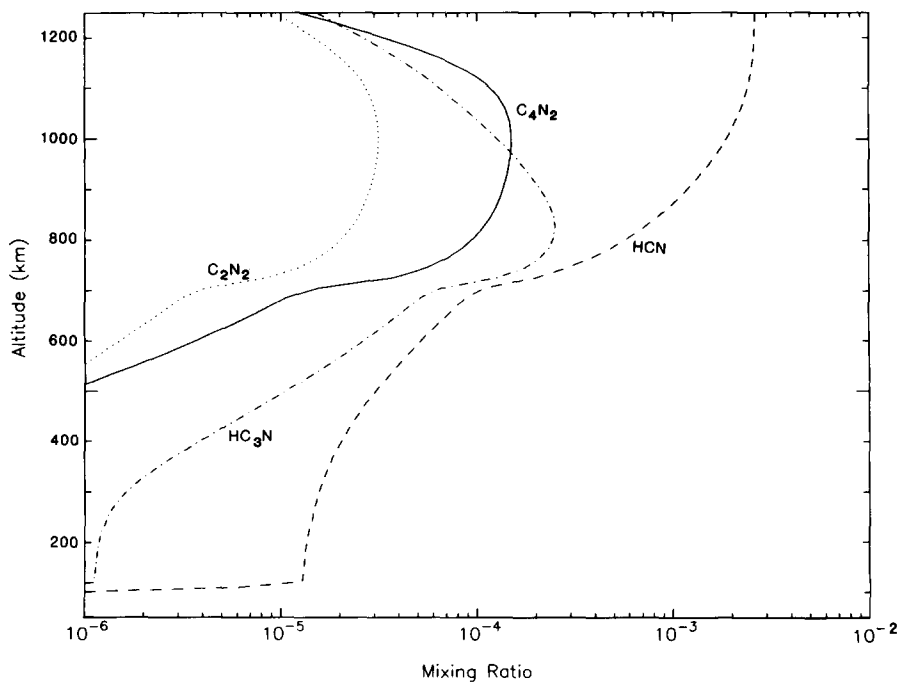


FIG. 1. Altitude profiles for the mixing ratios of HCN, HC_3N , C_2N_2 , and C_4N_2 computed with rate coefficients given in Table I.

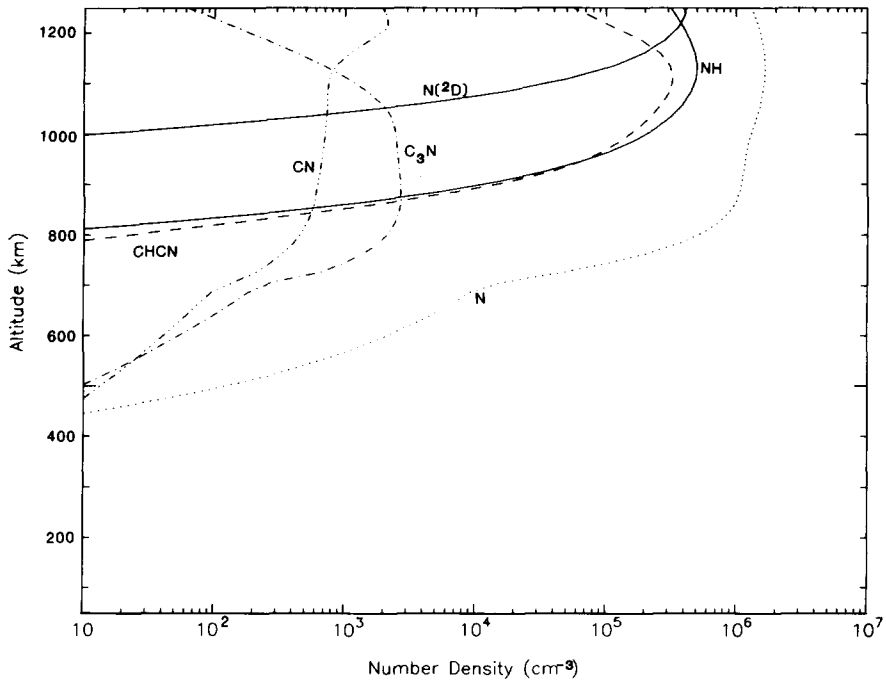


FIG. 2. Altitude profiles for the number densities of N, ($N(2D)$), NH, CN, CHCN, and C_3N , computed as for Fig. 1.

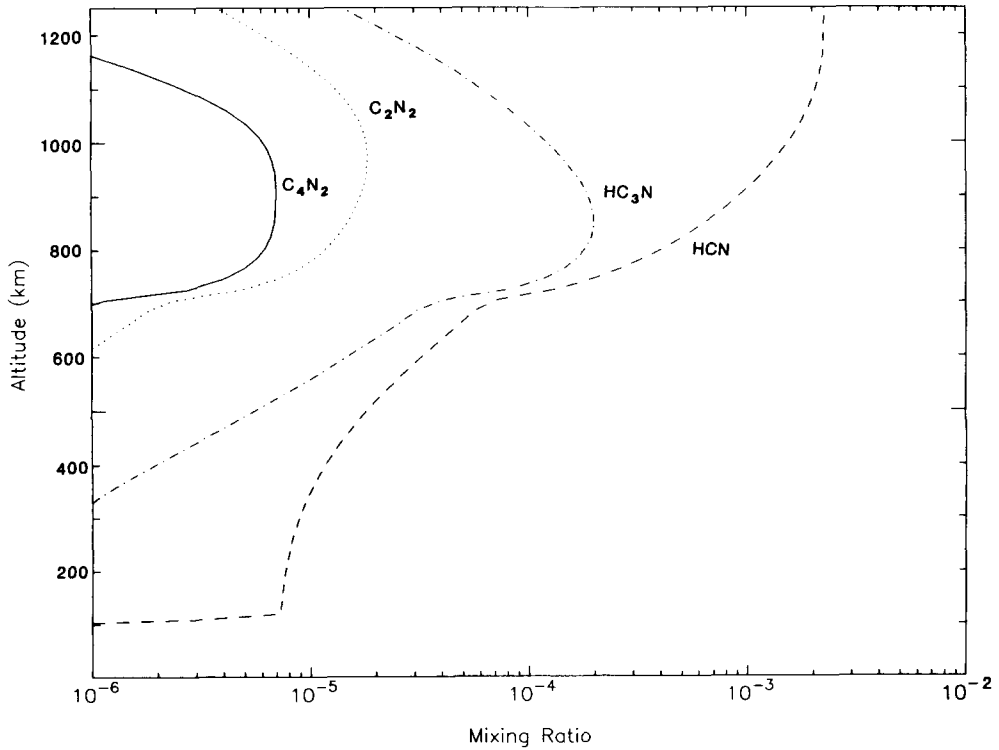


FIG. 3. Same as Fig. 1, except $k_2 = 1 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ and $k_4 = 5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ (see text).

substitution reaction, must be the most important. There are at least two other pieces of circumstantial evidence in support of this conclusion. First, channel (5) is analogous to the substitution reaction



which has a fast rate constant $k_6 = 2.3 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ (Schacke *et al.* 1977, Lichtin and Lin 1986). Second, C_2H_2 has two H atoms. In channel (5), one of the H atoms is replaced by CN; in channel (6) the other H atom is also replaced by CN. The two processes must be closely related and we can consider one as the counterpart of the other.

Photochemical model. The standard chemistry of nitrogen species on Titan is summarized in Table 3c of Yung *et al.* (1984). Table I lists the relevant revisions. The revised models is run with similar assumptions and boundary conditions as in Yung *et al.* (1984) except that the downward flux of NH at the upper boundary is set to zero, and instead we have a downward flux of $10^9 \text{ cm}^{-2} \text{ sec}^{-1} \text{ N}(\text{D})$ atoms (see Table 4 of Yung *et al.* 1984).

Figure 1 summarizes the altitude profiles of the important nitrile compounds HCN, HC_3N , C_2N_2 , and C_4N_2 . The concentrations of HCN, HC_3N , and C_2N_2 are close to those computed by Yung *et al.* (1984). However, the principal source of C_2N_2 in the current model is R3 instead of R1, as was in the old model (Table I). The computed results for C_4N_2 are new. C_4N_2 is formed primarily by R4 with a smaller contribution from R5. The major loss of C_4N_2 is photolysis (R7), followed by R8 and R9, leading to the formation of HC_3N . The concentrations of the odd nitrogen radicals N, $\text{N}(\text{D})$, NH, CN, and C_3N are shown in Fig. 2. Since there is considerable uncertainty in estimating the rate coefficients for the reactions R2 and R4, we have made runs using slower rate constants $k_2 = 1 \times 10^{-12}$ and $k_4 = 5 \times 10^{-12}$. The results are shown in Fig. 3.

We notice that the concentrations of C_2N_2 and C_4N_2 in the lower regions of the atmosphere are somewhat less than that required to explain the Voyager observations. Although these compounds are readily produced in the upper atmosphere, they are also readily destroyed by photolysis. Hence, few of these molecules can actually survive the transport from the upper atmosphere to the lower atmosphere. However, in the polar region in winter, transport to the lower atmosphere may be enhanced. Due to the high sphericity of Titan's atmosphere (radius 2575 km, mesosphere at $\sim 1000 \text{ km}$), the thin-shell approximation, which is appropriate for the atmospheres of the terrestrial planets, is not valid. An unusual geometrical configuration exists at the pole of Titan (see Figs. 4a and 4b). During the polar night, the mesosphere is exposed to sunlight and energetic electrons of magnetospheric origin. HCN and other nitrile compounds are being made and can diffuse downward into the polar cap

stratosphere, which stays in the shadow of the pole of Titan. This process can lead to the accumulation of enormous quantities of HCN and other species during the winter. The scenario is like that of O_3 in the Earth's stratosphere. O_3 has a maximum in the spring at high latitude even though O_3 is preferentially made at the equator (see, for example, Brasseur and Solomon 1984). The polar region acts as an effective storage for O_3 . In the early Titan spring, the time of the Voyager observations, the chemical time constants may be such that depletion has not yet had enough time to modify the high concentration of nitrile compounds, thus explaining the observations at 75°N lat. However, to study this problem realistically requires a two-dimensional photochemical model and is beyond the scope of this work.

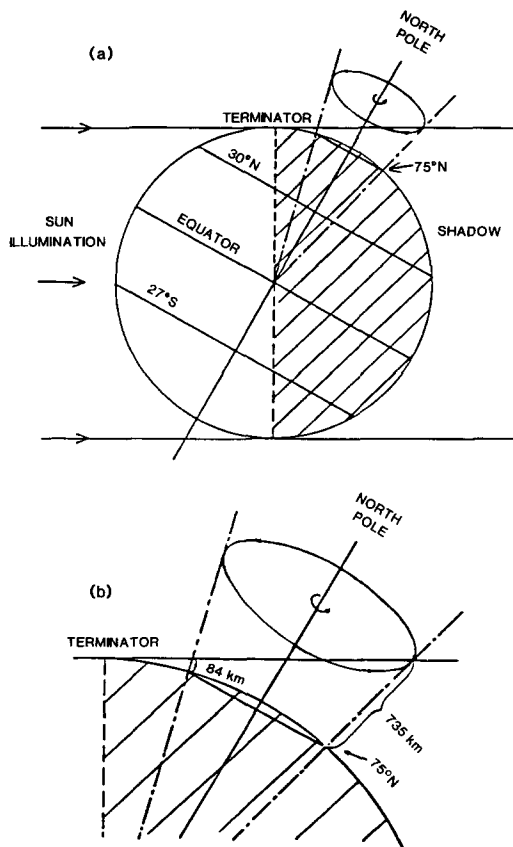


FIG. 4. The impact of sphericity of the Titan atmosphere on the photochemical model. (a) At the Titan winter solstice when the subsolar point is at 27°S lat, the "surface" of Titan north of 63°N is in darkness throughout the course of the Titan day. (b) At 75°N lat, the atmosphere up to 84 km above the 20-mbar level is in darkness throughout the course of a Titan day at winter solstice. Above 735 km from the surface, the atmosphere is illuminated by sunlight.

Conclusion. In this short note several new reactions are postulated (see Table I) and explored in our photochemical model. The predicted concentrations of the simple nitrile compounds are of the correct order of magnitude to explain the Voyager observations. We hope that this will provide some motivation for the kinetics community to devise experiments to measure the rate coefficients of some of our proposed reactions.

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