

# ORGANIC SYNTHESSES FROM CH<sub>4</sub>-N<sub>2</sub> ATMOSPHERES: IMPLICATIONS FOR TITAN\*

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(Received 16 November, 1981; in revised form 19 February, 1982)

**Abstract.** Numerous experiments have already been performed, simulating the evolution of gaseous mixtures containing CH<sub>4</sub> when submitted to energy flux. From their results, it appears that a variety of organic compounds, including unsaturated hydrocarbons and nitriles such as HCN, can be synthesized into noticeable amounts from CH<sub>4</sub>-N<sub>2</sub> mixtures. In particular, systematic studies of the influence of the composition of the mixture on the nature and amount of synthesized compounds show that organic volatile nitriles, and particularly cyanoacetylene and cyanogen, are formed only in media rich in nitrogen. Those nitriles have been identified very recently in the atmosphere of Titan, and thus, data from such laboratory experiments may provide important indirect information on the organic chemistry occurring at the periphery of this satellite of Saturn. However, during these experiments, there is a continuous formation and accumulation of molecular hydrogen, which does not occur in the atmosphere of Titan, because of H<sub>2</sub> escape. In order to reassess the data already available from this type of laboratory studies, experiments on CH<sub>4</sub>-N<sub>2</sub> atmospheres, with and without H<sub>2</sub> escape, have been recently performed. The influence of this parameter on the chemical evolution of the atmosphere and on the nature and relative quantities of organic compounds has been studied.

After reviewing these experiments, implications of the obtained results on the organic chemistry at the periphery of Titan are discussed.

## 1. Introduction

Before the Voyager mission, Titan was already considered as a very interesting body in the solar system, by scientists involved in the field of chemical evolution, organic cosmochemistry and exobiology (Chang *et al.*, 1979). It has been known that this satellite has an atmosphere (Kuiper, 1944), and that its atmosphere includes large quantities of methane (Kuiper, 1944; Trafton, 1972), suggesting it was reducing. In addition, very large quantities of H<sub>2</sub> in Titan's atmosphere seemed to be very unlikely (Münch *et al.*, 1977), because of its escape (Münch *et al.*, 1977; Hunten, 1978). These conditions are expected to be favorable for atmospheric organic syntheses.

There has been a tremendous amount of experimental work simulating organic synthesis in various model atmospheres submitted to different energy sources. For most of them, the main goal was to simulate chemical evolution of the periphery of the primitive Earth in order to determine the nature and, eventually, the relative quantities of organics produced by the energy flux. The results of these experiments show that reducing atmospheres, or slightly reducing atmospheres where carbon is in the form of CH<sub>4</sub>, such as CH<sub>4</sub>-NH<sub>3</sub> or CH<sub>4</sub>-N<sub>2</sub> mixtures, favor production of organics, and especially of N-containing organic compounds, more than oxidizing or even neutral atmospheres where carbon is mainly in the form of CO<sub>2</sub>.

In fact, this can be theoretically expected from simple thermodynamical calculation.

\* Paper presented at the 6th College Park Colloquium, October 1981.

For instance, by considering the standard free enthalpy of synthesis of organic compounds from different media containing C–H–N–O (Toupance *et al.*, 1971).  $\Delta G^\circ f$  is always much lower (and thus, the related chemical reactions are less difficult) starting from a reducing atmosphere such as  $\text{CH}_4\text{--N}_2\text{--(H}_2\text{O)}$  or  $\text{CH}_4\text{--NH}_3\text{--(H}_2\text{O)}$  than from an oxidizing or neutral atmosphere  $\text{CO}_2\text{--N}_2\text{--H}_2\text{O}$ .

There are still controversies about the nature of the main components of the primitive atmosphere of the Earth, and it seems likely that the problem will remain open for a long time. But, in the case of Titan, the type of atmosphere is not any longer a question of speculation. It appears from the Voyager data that Titan's atmosphere is effectively slightly reducing since it is composed mainly of  $\text{N}_2$  (82–95 %), with noticeable molar fraction of  $\text{CH}_4$  (4–6 %), and a very small fraction of hydrogen ( $\leq 0.4$  %). Thus, all the experimental work which has been carried out so far on reducing atmosphere  $\text{CH}_4\text{--N}_2$ , may be reexamined now from a point of view of Titan. Their results, may provide some qualitative information on the nature of the organic compounds which can be expected in the periphery of Titan. For this reason, although it is a very practical approach, simulation experiments may be considered as complementary to theoretical modeling, of the type given in Strobel's (1982) presentation.

In the present paper, only the experimental work which has been carried out on organic synthesis from  $\text{CH}_4\text{--N}_2$  atmospheres will be reviewed. We will also include some new results, in which hydrogen escape is simulated. Then, the possible applications of these findings to Titan will be discussed.

## 2. Review

As a matter of fact, contrary to the case of  $\text{CH}_4\text{--NH}_3$  atmosphere, only a few simulation experiments have been carried out, so far, on  $\text{CH}_4\text{--N}_2$  atmospheres. In these experiments UV light, high energy electrons and protons, and electrical discharges were used as energy sources (Table I).

### 2.1. UV LIGHT

The photochemistry of methane has been extensively studied, both experimentally and theoretically. In particular Titan's hydrocarbon chemistry has been studied theoretically in detail by Strobel (1974, 1982).  $\text{CH}_4$  absorbs UV wavelengths shorter than  $\approx 150$  nm. Irradiation of  $\text{CH}_4$  at  $\lambda \leq 147$  nm allows the production of hydrocarbons, mainly saturated, up to  $\text{C}_5$ , the major products being  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_3\text{H}_8$ . For instance, Bossard (1979), Bossard and Toupance (1980), Bossard *et al.* (1981) using a 147 nm light, found that the ratio of unsaturated  $\text{C}_2$ /saturated  $\text{C}_2$  is equal to 0.5 and unsaturated  $\text{C}_3$ /saturated  $\text{C}_3$  is equal to 0.2.

Prolonged irradiation of  $\text{CH}_4$  can give rise to polymers (mainly acetylene polymers), which has been invoked as a possible constituent of the chemical haze in Titan's atmosphere (Podolak *et al.*, 1979 and included references).

There has been only one report of a photochemical experiment, which was successful in term of synthesis of N-containing organic compounds (Table I), by Dodonova (1966).

TABLE I  
Simulation experiments on CH<sub>4</sub>-N<sub>2</sub> model atmospheres

Energy source	Authors	Reported products in the gas phase
<i>UV Light</i>		
125–170 nm	Dodonova (1966)	HCN
123.6 nm	Bragin and Nicoll (1976) from Chang <i>et al.</i> (1979)	no N-Contg organics
123.6 nm	Burke (1977)	ibidem
147 nm	Bossard (1978)	ibidem
184.9 nm	Ferris and Chen (1975)	ibidem
<i>High energy particles</i>		
Protons 2 MeV	Scattergood <i>et al.</i> (1974, 1975)	C <sub>2</sub> , C <sub>3</sub> hydrocarbons C <sub>4</sub> H <sub>2</sub> , CH <sub>3</sub> CN
Electrons 17 MeV	Balestic (1974)	C <sub>2</sub> , C <sub>3</sub> hydrocarbons HCN, CH <sub>3</sub> CN, C <sub>2</sub> H <sub>5</sub> CN no amine
<i>Electrical discharges</i>		
Spark (Closed System) P ≈ 1 atm	Sanchez <i>et al.</i> (1966)	C <sub>2</sub> H <sub>6</sub> , C <sub>4</sub> H <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> HCN and CH ≡ C-CN
Corona – (Flow System) P = 20 Torr	Toupance <i>et al.</i> (1971, 1975)	C <sub>2</sub> –C <sub>4</sub> hydrocarbons, C <sub>6</sub> H <sub>6</sub> HCN CH <sub>3</sub> CN, C <sub>2</sub> H <sub>5</sub> CN, (CN) <sub>2</sub> CH <sub>2</sub> = CH – CN, CH ≡ C-CN
Spark – (open System) P ≈ 150 Torr	Mourey <i>et al.</i> (1982)	ibidem

After 10 hours irradiation of mixtures containing CH<sub>4</sub>-N<sub>2</sub> (I–I) at 5–8 Torr and 100–200 Torr total pressure, with a hydrogen lamp (125–170 nm), the author identified in the low pressure sample, HCN (the limit of detectability of this compounds, with the analytical techniques which were used, was as low as about 20 nmoles). She explains its formation by the possible photoactivation of N<sub>2</sub> and its interaction with CH radicals resulting from the decomposition of CH<sub>4</sub>.

It must be pointed out that several attempts have been made at the NASA's Ames Research Center (Chang *et al.*, 1979), and at the California Institute of Technology (Burke, 1977), to duplicate this experiment (but with a monochromatic hydrogen lamp = 123.6 nm), and no HCN or N-containing organics were detected. Photochemical experiments performed with UV light of higher wavelengths did not produce any detectable N-containing organic compound (Bossard, 1979; Bossard *et al.*, 1981; Ferris and Chen, 1975).

So far, it seems that the main role of UV light in the production of organics from a CH<sub>4</sub>-N<sub>2</sub> atmosphere must be the photosynthesis of hydrocarbon chains from CH<sub>4</sub>.

## 2.2. HIGH ENERGY PARTICLES

The problem of organic syntheses on Titan from high energy particles has been recently

studied theoretically by Capone *et al.* (1980, 1981). They propose that the reaction  $N^* + CH_4 \rightarrow HCN + H_2 + H$  could be an important source of HCN on Titan. The only experimental work which has been specifically carried out in order to simulate the production of organic molecules on Titan from  $CH_4-N_2$  mixtures used high energy proton irradiation. It was performed by Scattergood *et al.* (1974, 1975) who irradiated with a Van de Graaf accelerator several mixtures, including  $CH_4-NH_3$  and  $CH_4-N_2$  (I-I) at high pressure ( $\approx 600$  Torr). After 3 to 6 hours irradiation, they analyzed the gaseous phase, and the condensed phase (a brown-orange liquid). In the case of  $CH_4-NH_3$ , they detected  $C_2$  and  $C_3$  hydrocarbons,  $C_4H_2$  and  $CH_3CN$ . They did not search for HCN. Analysis of the orange-brown polymer shows evidence for alkyl hydrocarbons and amines, hexamethylene tetramine and its methyl and dimethyl homologues. Concerning the  $CH_4-N_2$  experiment, the authors only mention that the same products were formed, but the cyclic amines were in smaller amount. In fact, it must be pointed out that, because of the nature of the accelerated particles (H), the molar ratio of ammonia or of its dissociated species, NH and  $NH_2$ , during the experiment on the  $CH_4-NH_3$  mixture, may have been quite high (due to reactions such as  $N_2 + H \rightarrow NH + N$ ).

The same kind of experiment has been carried out in France, by Balestic, who used high energy electrons from a linear accelerator. Although the only available reference of this work is a Ph.D. thesis, the obtained results are significant (Balestic, 1974). Irradiation of  $CH_4-N_2$  (I-I) at high pressure (720 Torr) gives rise to hydrocarbons, mainly  $C_2H_6$  and  $C_3H_8$ , and nitriles; HCN,  $CH_3CN$  and  $C_2H_5CN$ . Similar experiments done with  $CH_4-N_3$  initial mixtures gave noticeably smaller radiochemical yields of nitriles. In addition, amines were detected only in the  $CH_4-NH_3$  experiments. Balestic analyzed the condensed material and found the presence of oligomers with molecular weight up to 970. Infrared analysis shows the presence of  $-CN$ ,  $-CH_2-NH-$ ,  $-CH=N-$  groups. Contrary to the results obtained with  $CH_4-NH_3$ , no  $-NH_2$  or  $C=NH$  seems to be included in the condensed material and its acid hydrolysis does not release any detectable amino acids.

If the results concerning the composition of this polymeric material seems to be quite different from one experiment to another, the data related to the products with low molecular weight, present in the gas phase, are more reproducible. This is very clear if we examine experiments, using electrical discharges.

### 2.3. ELECTRICAL DISCHARGES

The first simulation experiment on  $CH_4-N_2$  atmosphere was carried out, with electrical discharge, in 1966, by Sanchez *et al.* (1966). They reported the formation of  $C_2H_6$ ,  $C_4H_2$ , HCN and  $CH \equiv C-CN$  as the major products from mixtures of  $CH_4-N_2$  (I-4) at  $\approx 1$  atm pressure. They noticed that  $CH \equiv C-CN$  was always the most abundant nitrile after HCN in their experiments, except when  $NH_3$  was present in place of  $N_2$ .

A very similar observation was reported from simulation experiments carried out in our laboratory, with Corona discharge (Toupance, 1973; Toupance *et al.*, 1975). Mixtures  $CH_4-N_2$  and  $CH_4-NH_3$  of various compositions were submitted to a low pressure (20 Torr) silent discharge for few seconds. The resulting effluents were analyzed by

several techniques. We reported the formation of saturated and unsaturated hydrocarbons, up to C<sub>4</sub> (mainly C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>2</sub>), and the formation of nitriles: HCN, (CN)<sub>2</sub>, CH≡C-CN, CH<sub>3</sub>-CN, C<sub>2</sub>H<sub>5</sub>CN and CH<sub>2</sub>=CH-CN. Figure 1 represents the variation

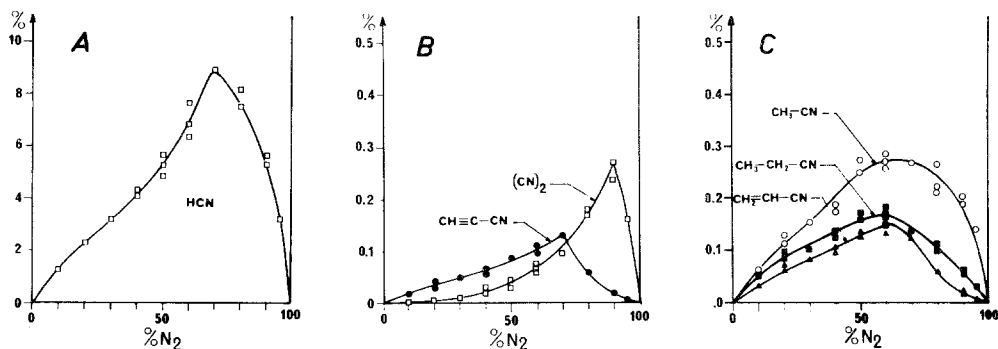


Fig. 1. Molar ratio of several nitriles in effluents resulting from subjecting CH<sub>4</sub>-N<sub>2</sub> mixtures (20 Torr) to a corona glow discharges (3 seconds), as a function of the molar ratio of N<sub>2</sub> in the initial mixture. A: hydrogen cyanide; B: cyanogen and cyanoacetylene; C: acetonitrile, propionitrile and acrylonitrile.

of the molar ratio of these compounds as a function of the N<sub>2</sub> percentage. It can be seen that the molar ratio, for all the N-containing compounds is maximum in N<sub>2</sub> rich media. Even a mixture containing initially 5% CH<sub>4</sub> - 95% N<sub>2</sub> allows the production of noticeable amount of nitrile. In fact, as can be seen on Figure 2, the yield of HCN relative to

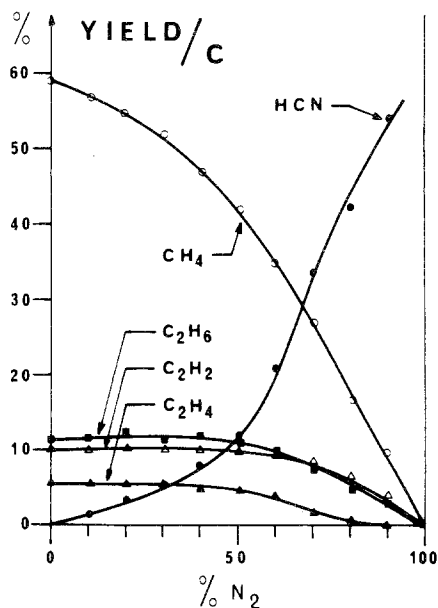


Fig. 2. Yield of synthesis of several compounds in effluents, relatively to the initial carbon content, as a function of the molar ratio of N<sub>2</sub> in the initial CH<sub>4</sub>-N<sub>2</sub> mixture (same discharge conditions than for Figure 1).

the initial carbon content increases continuously when the molar ratio of  $\text{CH}_4$  in the initial  $\text{CH}_4\text{-N}_2$  mixture decreases.

Studies on  $\text{CH}_4\text{-NH}_3$ , using the same conditions, show no  $(\text{CN})_2$  and almost no  $\text{CH}\equiv\text{C-CN}$  in the effluent gases, whatever is the relative composition of the initial mixture. Let us mention that from similar studies on  $\text{CH}_4\text{-N}_2$  and  $\text{NH}_3$  mixtures including various amounts of  $\text{H}_2\text{S}$  (Raulin and Toupance, 1975; 1976), it can be assumed that small amounts of  $\text{H}_2\text{S}$  (up to  $\approx 5\%$ ) would not significantly change those results. The same kind of studies have also been carried out on tertiary mixtures  $\text{CH}_4\text{-N}_2\text{-H}_2$  (Toupance, 1973). The yield of synthesis of HCN is not noticeably affected by the presence of very large quantities of  $\text{H}_2$ . The yield of nitriles with unsaturated carbon chains such as  $\text{CH}_2=\text{CH-CN}$  and  $\text{CH}\equiv\text{C-CN}$ , and of  $(\text{CN})_2$  is slightly decreased, while the opposite is observed for the other nitriles, as shown on Figure 3.

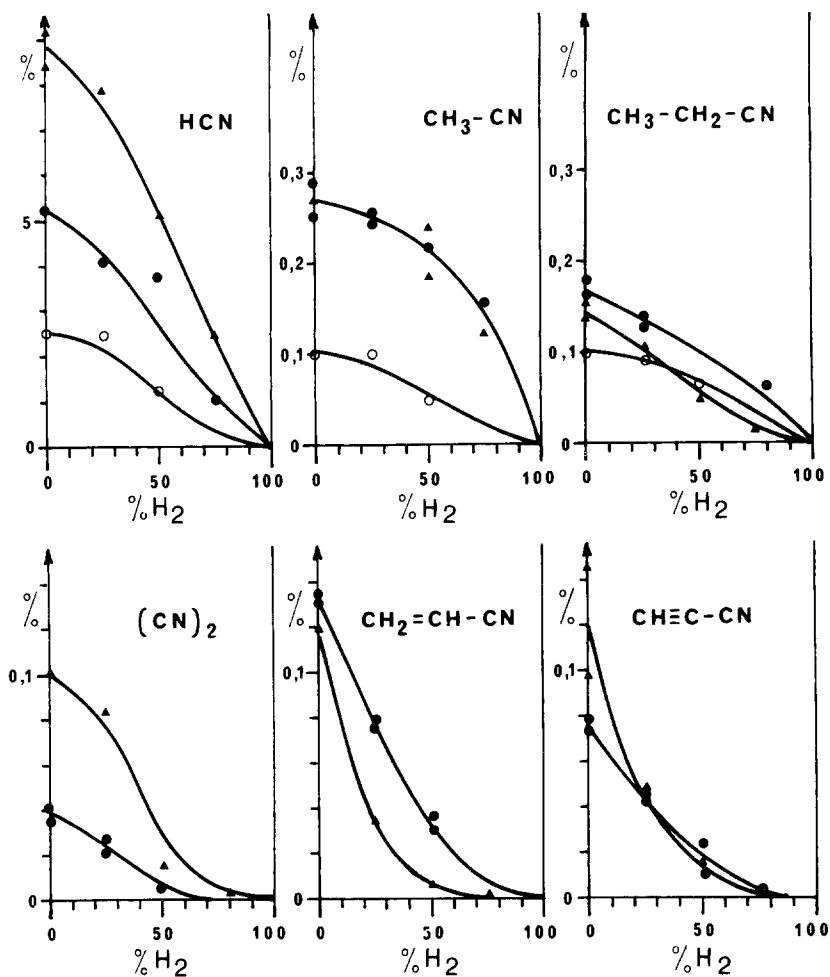


Fig. 3. Molar ratio of several nitriles in effluents, resulting from subjecting  $\text{CH}_4\text{-N}_2\text{-H}_2$  mixtures to a corona glow discharge (same conditions than for Figure 1), as a function of the molar ratio of  $\text{N}_2$  in the initial mixture, and for different initial value of  $\text{CH}_4/\text{N}_2$ :  $\circ$ :  $\text{CH}_4/\text{N}_2 = 3$ ;  $\bullet$ :  $\text{CH}_4/\text{N}_2 = 1$ ;  $\blacktriangle$ :  $\text{CH}_4/\text{N}_2 = 1/3$ .

2.4. EFFECT OF H<sub>2</sub> ESCAPE

Now, what will happen, on the contrary, if the molar ratio of H<sub>2</sub> in the model atmosphere remains very small? In all the reviewed experiments, there is always H<sub>2</sub> present in significant amount due to the cracking of CH<sub>4</sub>, even in the experiments performed with corona discharge, where the system is an open system. Accumulation of molecular hydrogen during the experiment does not fit with a plausible model of a reducing atmosphere of a small body like the Earth or Titan. In spite of the low temperature of Titan's exosphere, it seems very likely that the rate of H<sub>2</sub> escape is sufficiently high to maintain a very low molar ratio in its atmosphere (i.e., < 10<sup>-2</sup>). A series of simulation experiments using spark discharge has recently been carried out in our laboratory in order to estimate the possible influence of H<sub>2</sub> escape on the formation of atmospheric organic molecules (Toupance *et al.*, 1978; Mourey *et al.*, 1981; Mourey, 1982).

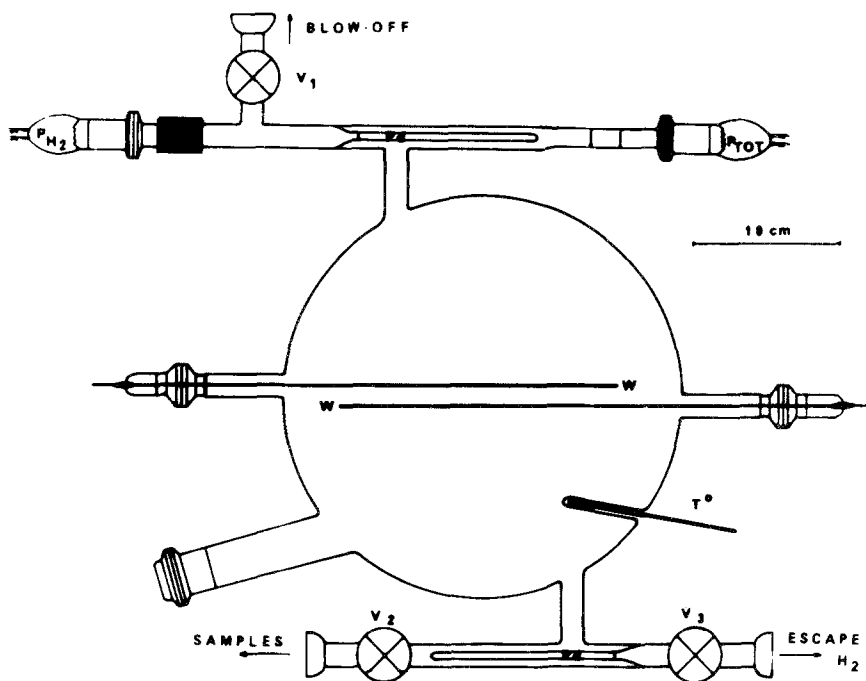


Fig. 4. Experimental device used for simulating H<sub>2</sub> escape, with two palladium membranes (the two fingers, at the top and at the bottom).

In particular, we have just completed the study of CH<sub>4</sub>-N<sub>2</sub> mixtures. These studies have been performed with the help of a reactor (Figure 4) having 2 palladium membranes, allowing the simulation of the escape. When heated at 245°C, the membranes are permeable to H<sub>2</sub> which is pumped out of the reactor, selectively. Without pumping out through the Pd membranes, H<sub>2</sub> remains in the reactor. Experiments have been carried out on CH<sub>4</sub> (50 Torr) and CH<sub>4</sub> (50 Torr)-N<sub>2</sub> (100 Torr) mixtures, with and without H<sub>2</sub> escape.

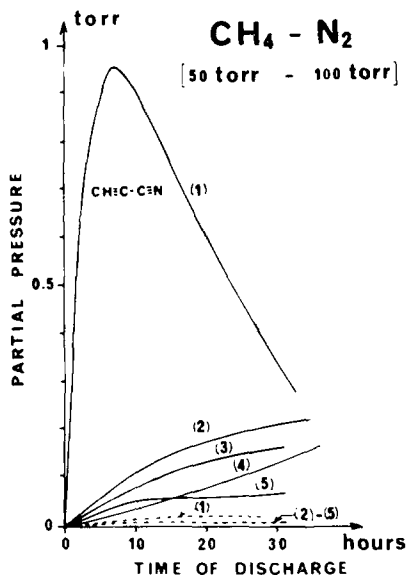


Fig. 5. Partial pressure of some synthesized nitriles as a function of the time of discharge in the reactor.

(————— : with hydrogen escape; - - - - - : without hydrogen escape)  
 1:  $\text{CH}\equiv\text{C}-\text{CN}$ ; 2:  $\text{CH}_3\text{CN}$ ; 3:  $\text{CH}_2=\text{CH}-\text{CN}$ ; 4:  $(\text{CN})_2$ ; 5:  $\text{C}_2\text{H}_5\text{CN}$ .

Samples of the mixtures collected after different sparking times have been analyzed, and the curves representing the variation of the partial pressure of the products as a function of the sparking time have been obtained. As an example, Figure 5 shows the results

TABLE II  
 Initial overall rates in mole  $\text{cm}^{-3} \text{s}^{-1}$

$\text{CH}_4$ (50 Torr)		
Compounds	Without $\text{H}_2$ escape	With $\text{H}_2$ escape
$\text{CH}_4$	$-5.5 \times 10^{-11}$	$-10^{-10}$
$\text{C}_2\text{H}_6$	$\approx 6.0 \times 10^{-12}$	$1.2 \times 10^{-11}$
$\text{C}_2\text{H}_2$	$\approx 3.0 \times 10^{-12}$	$6.0 \times 10^{-12}$
$\text{C}_2\text{H}_4$	$4.5 \times 10^{-12}$	$6.0 \times 10^{-12}$
$\text{C}_3\text{H}_6$	$6.5 \times 10^{-13}$	$6.2 \times 10^{-13}$
$\text{C}_3\text{H}_8$	$5.1 \times 10^{-13}$	$6.1 \times 10^{-13}$
$\text{CH}_3-\text{C}\equiv\text{CH}$	$1.9 \times 10^{-13}$	$3.5 \times 10^{-13}$
$\text{CH}_2=\text{C}=\text{CH}_2$	$5.5 \times 10^{-14}$	$9.0 \times 10^{-14}$
$\text{C}_4\text{H}_8$ (mixture)	$2.8 \times 10^{-13}$	$1.8 \times 10^{-13}$
$\text{CH}\equiv\text{C}-\text{C}_2\text{H}_5$	$9.0 \times 10^{-14}$	$1.5 \times 10^{-13}$
iso $\text{C}_4\text{H}_{10}$	$6.0 \times 10^{-14}$	—
$\text{C}_4\text{H}_2$	$5.5 \times 10^{-14}$	$3.3 \times 10^{-13}$
$\text{C}_6\text{H}_6$	$5.1 \times 10^{-15}$	$1.4 \times 10^{-14}$

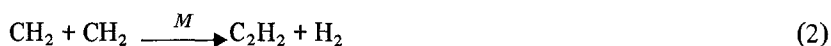


TABLE III  
 Initial overall rates in mole · cm<sup>-3</sup> s<sup>-1</sup>

Compounds	Without escape		With H <sub>2</sub> escape
	CH <sub>4</sub> (50 Torr)	CH <sub>4</sub> -N <sub>2</sub> (50 Torr)-(100 Torr)	CH <sub>4</sub> -N <sub>2</sub> (50 Torr)-(100 Torr)
CH <sub>4</sub>	-5.5 × 10 <sup>-11</sup>	-1.4 × 10 <sup>-10</sup>	-9.7 × 10 <sup>-11</sup>
N <sub>2</sub>		-1.9 × 10 <sup>-11</sup>	-2.8 × 10 <sup>-11</sup>
H <sub>2</sub>	5.9 × 10 <sup>-11</sup>	2.1 × 10 <sup>-10</sup>	
C <sub>2</sub> H <sub>2</sub>	≈ 3.0 × 10 <sup>-12</sup>	2.9 × 10 <sup>-11</sup>	4.1 × 10 <sup>-11</sup>
C <sub>2</sub> H <sub>6</sub>	≈ 6.0 × 10 <sup>-12</sup>	5.8 × 10 <sup>-12</sup>	5.4 × 10 <sup>-12</sup>
C <sub>2</sub> H <sub>4</sub>	4.5 × 10 <sup>-12</sup>	2.3 × 10 <sup>-12</sup>	3.1 × 10 <sup>-12</sup>
C <sub>3</sub> H <sub>4</sub>	1.9 × 10 <sup>-13</sup>	2.2 × 10 <sup>-13</sup>	2.5 × 10 <sup>-12</sup>
C <sub>3</sub> H <sub>6</sub>	6.5 × 10 <sup>-13</sup>	1.9 × 10 <sup>-13</sup>	5.5 × 10 <sup>-13</sup>
C <sub>3</sub> H <sub>8</sub>	5.1 × 10 <sup>-13</sup>	6.2 × 10 <sup>-14</sup>	2.7 × 10 <sup>-13</sup>
CH <sub>2</sub> =C=CH <sub>2</sub>	5.5 × 10 <sup>-14</sup>	8.3 × 10 <sup>-14</sup>	8.9 × 10 <sup>-14</sup>
C <sub>4</sub> H <sub>2</sub>	5.5 × 10 <sup>-14</sup>	2.5 × 10 <sup>-12</sup>	3.5 × 10 <sup>-14</sup>
C <sub>6</sub> H <sub>6</sub>	5.1 × 10 <sup>-15</sup>	2.8 × 10 <sup>-14</sup>	2.9 × 10 <sup>-14</sup>
NH <sub>3</sub>		1.8 × 10 <sup>-13</sup>	< 10 <sup>-15</sup>
HCN		7.6 × 10 <sup>-12</sup>	1.2 × 10 <sup>-11</sup>
CH≡C-CN		1.4 × 10 <sup>-14</sup>	1.7 × 10 <sup>-12</sup>
CH <sub>2</sub> =CH-CN		1.2 × 10 <sup>-14</sup>	1.4 × 10 <sup>-13</sup>
(CN) <sub>2</sub>		5.1 × 10 <sup>-15</sup>	4.8 × 10 <sup>-14</sup>
CH <sub>3</sub> CN		< 10 <sup>-15</sup>	1.5 × 10 <sup>-13</sup>
C <sub>2</sub> H <sub>5</sub> CN		< 10 <sup>-15</sup>	8.3 × 10 <sup>-14</sup>

related to some nitriles. The dashed curves correspond to the experiment without H<sub>2</sub> escape. It seems clear that, with H<sub>2</sub> escape, there is a tremendous increase in the production of nitriles, and, particularly, of cyanoacetylene. Now, in order to compare more quantitatively the different results, let us consider only the very beginning of the irradiation, by taking into account the initial slope of the curves. This slope, *k*, represents the initial rate of the overall reaction of formation or destruction of a given compound. Table II shows the initial rate for the various compounds identified in the mixtures obtained after sparking of CH<sub>4</sub> alone, with and without H<sub>2</sub> escape. By comparing these values no major difference appears between the two experiments, except for C<sub>4</sub>H<sub>2</sub>, the rate of which is almost 10 times greater when H<sub>2</sub> escapes.

Now, if we consider the results related to CH<sub>4</sub>-N<sub>2</sub> mixtures on Table III, the differences are much greater. First, we can estimate the influence of the presence of N<sub>2</sub> and the total pressure by comparing the results of the experiments without H<sub>2</sub> escape on CH<sub>4</sub> alone (50 Torr) and CH<sub>4</sub>-N<sub>2</sub> (100 Torr). The initial rates of production of H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>4</sub>H<sub>2</sub> are 1 or 2 orders of magnitude greater when N<sub>2</sub> is present. This may be explained by assuming that the main reaction forming these molecules are given in the three-body reaction:



It must be pointed out, that similar studies on  $\text{CH}_4$  alone at higher pressures, show, qualitatively, a similar effect of the total pressure on the initial rate of formation of these three products. However, the observed increase is higher when  $\text{N}_2$  is used in place of  $\text{CH}_4$ , so that the pressure effect is not sufficient to explain this phenomenon.

Now, if we compare the results of the experiments carried out on  $\text{CH}_4 - \text{N}_2$  with and without  $\text{H}_2$  escape, the rate of formation of hydrocarbons and HCN are mainly the same, except in the case of  $\text{C}_4\text{H}_2$ , the rate of which is almost 100 times smaller when  $\text{H}_2$  escapes. On the contrary, the rate of all the other nitriles are much higher, with  $\text{H}_2$  escape: from one order of magnitude to 2 orders in the case of  $\text{CH} \equiv \text{C} - \text{CN}$ . This drastic increase of the rate of cyanoacetylene can be correlated to the decrease of  $\text{C}_4\text{H}_2$ , by assuming that the main reaction of formation of  $\text{C}_3\text{NH}$  is:



When  $\text{H}_2$  does not escape, the steady state concentration of CN is lower and the rate of (4) may be small enough to allow reaction (3) to be significant.

### 3. Conclusions

It is very likely that in Titan's atmosphere high energy particles such as electrons and protons, from cosmic rays, from the solar wind or the Saturn wind, and UV light, contribute in the production of hydrocarbons. But, as already mentioned by Chang *et al.* (1979), and theoretically described by Capone *et al.* (1980, 1981), only high energy particles are probably mainly involved in the formation of C-N bond.

Electrical discharges have not been detected by Voyager in Titan's atmosphere. In addition, the temperature of Titan's environment is much lower than the temperature used in all the simulation experiment that we have reviewed here. However, the data available from the experiments carried out with electrical discharge, may have a bearing on our understanding of the organic chemistry of Titan, at least to anticipate the nature of the main organic compounds at Titan's periphery.

From these results, it appears that saturated and unsaturated hydrocarbons from  $\text{C}_2$  to  $\text{C}_4$  and nitriles as the only major N-containing organic compounds should be present in noticeable amount in Titan's atmosphere. The absence of amines is also in very good agreement with the results of UV experiments recently carried out on  $\text{CH}_4 - \text{NH}_3$  mixtures of various compositions (Bossard, 1979; Bossard and Toupance, 1980). They have shown that amines are formed only from  $\text{NH}_3$ -rich mixtures; otherwise, nitriles are the only N-containing organic compounds in the gas phase, even in the presence of high  $\text{H}_2$ -dilution (Raulin *et al.*, 1979). From the simulation experiments carried out on  $\text{CH}_4 - \text{N}_2$  mixtures with  $\text{H}_2$ -escape, the nitriles listed on Table IV can be expected. At

temperatures of 150 K or higher (Titan's total atmospheric pressure  $\leq 10$  mb), the vapor pressure of these compounds is not negligible, and can be high enough to provide a sufficient molar ratio in the atmosphere, to be detectable. Let us mention that C<sub>2</sub>H<sub>5</sub>CN has also been very recently proposed by Capone *et al.* (1981) as a plausible candidate for Titan's atmosphere, from theoretical considerations.

TABLE IV

Nitriles expected in Titan's atmosphere from simulation experiment	Maximum vapor pressure (order of magnitude) in mb at 150 K	Effective molar ratio from IRIS
HCN	10 <sup>-2</sup>	2.10 <sup>-7</sup>
CH $\equiv$ C-CN	$\approx 10^{-3}$ -10 <sup>-4</sup>	10 <sup>-8</sup> -10 <sup>-7</sup>
CH <sub>3</sub> -CN	10 <sup>-5</sup>	
CH <sub>2</sub> =CH-CN	10 <sup>-5</sup>	
(CN) <sub>2</sub>	10 <sup>-1</sup>	10 <sup>-8</sup> -10 <sup>-7</sup>
C <sub>2</sub> H <sub>5</sub> CN	10 <sup>-6</sup>	

Learning from the Voyager data that N<sub>2</sub> was the main component in Titan's atmosphere was extremely important. However the last identification made by the IRIS experiment (Hanel *et al.*, 1981; Kunde *et al.*, 1981) came not as a surprise, but as fantastic news. Imagine our happiness when we learned that the organic compounds we were expecting on Titan from simulation experiments had been effectively identified!

The detection of HCN, CH $\equiv$ C-CN and (CN)<sub>2</sub> is of very great importance, because of the various organic syntheses and photosyntheses (see, for instance, Ferris *et al.*, 1973; Schwartz, 1981; Oró and Lazcano-Araujo, 1982 and references therein), offered by these products. The other nitriles expected to be present in Titan's atmosphere may also give rise to the formation of organic molecules of higher molecular weight, by mechanisms involving addition reactions on the -C $\equiv$ N. A mechanism of this type has been previously suggested by Ponnampertuma (1976), in the case of CH<sub>3</sub>CN. Most of these small molecules, because of the presence of a -CN group, eventually conjugated with an unsaturated carbon chain, are high energy content species. They are the atmospheric precursors of several biochemical compounds, including purine and pyrimidine derivatives (see, for instance, Ferris and Joshi, 1978; Schwartz, 1981; Oró and Lazcano-Araujo, 1982; and references therein). On the primitive Earth, these precursors may have been preserved from further destruction in the atmosphere, because of their dissolution in the water of the oceans. The presence of a cold trap at the surface of Titan, may have played a comparable role, and may have allowed the accumulation of atmospheric precursors. Then, these could have slowly evolved at the low surface temperature, but this is another story....

In any case, the already detected presence of HCN, CH $\equiv$ C-CN and (CN)<sub>2</sub> in Titan's atmosphere is the sign that a relatively complex organic chemistry is occurring at its periphery. Titan can be actually considered as the first place of interest for exobiology in our solar system. Studies *in situ* are not expected in the near future. However, observa-

tion from an orbiter or from a satellite may provide very useful information about the organic constituents on Titan. Although such space missions currently represent wishful thinking on the part of much of the scientific community it is now already of great importance to collect any spectroscopic data concerning the organic compounds expected to be present on Titan, including data on the already detected nitriles and their derivatives and oligomers.

### Acknowledgement

We thank the Centre National de la Recherche Scientifique and the Institut National d'Astronomie et de Géophysique for support of this work, under grant number ATP 3754 (ATP Planétologie 1980).

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