

# FORMATION OF PREBIOCHEMICAL COMPOUNDS IN MODELS OF THE PRIMITIVE EARTH'S ATMOSPHERE

I:  $\text{CH}_4\text{—NH}_3$  and  $\text{CH}_4\text{—N}_2$  Atmospheres

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**Abstract.** In order to understand the formation of organic compounds in the primitive atmosphere, the first steps of evolution in models of the primitive atmosphere were investigated. Mixtures containing C—H—N elements were subjected to a low pressure silent electric discharge for several seconds, and the resulting effluents were analysed mainly by gas chromatography, infrared spectrometry and chemical analysis. The formation of hydrocarbons (i.e. ethylene, acetylene, methylacetylene) and of nitrogen containing compounds (i.e. hydrogen cyanide, cyanogen, saturated nitriles, acrylonitrile, cyanoacetylene) is reported. The influence of the initial mixture composition on the amount of compounds formed was systematically studied. The nature of the nitrogen source ( $\text{N}_2$  or  $\text{NH}_3$ ) in the primitive atmosphere has a great influence on the amount and on the very nature of the synthesized products. It is shown that important precursors such as cyanogen and cyanoacetylene are formed only in very rich  $\text{N}_2$  mediums. These results show the important role played by the nature of the primitive atmosphere in the determination of the chemical evolution pathways.

## 1. Introduction

During the formation of compounds of biological interest under primitive earth conditions, many simple molecules such as hydrogen cyanide, formaldehyde, or cyanoacetylene seem to play important roles. The formation of these molecules under possible primitive conditions has been frequently reported (Miller, 1957; Sanchez *et al.*, 1966). However, no extensive study has yet been performed to determine the range of composition of the primitive atmosphere which allows the formation of the principal key intermediates. We have presented at the Third International Conference on the Origin of Life (Pont à Mousson, 1970) several elements of our study which has the objective of giving a final answer to this problem (Toupance *et al.*, 1971). We now present the results obtained in studies concerning the compounds formed in atmospheres containing the elements C, H, and N. Results obtained from this laboratory (Toupance, 1973) and concerning oxygen-containing atmospheres will be reported elsewhere.

## 2. Experimental

In our experiments, models of primitive atmospheres of known composition enter with a well known flow rate into a reactor in which there is a low pressure (20 torr) corona discharge. The effluents are analysed, and the concentrations of the identified compounds are plotted as a function of the initial atmospheric composition.

The block diagram of our apparatus is given by Raulin and Toupance (1974). Figure 1 gives the diagram of the reactor. The anode is a 10 cm long brass tube,

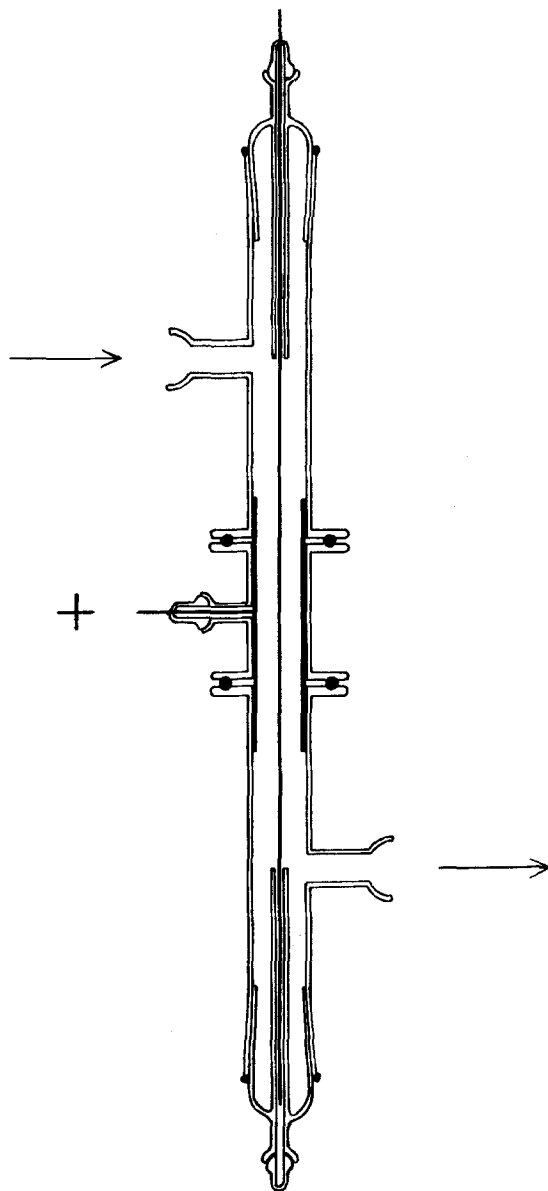


Fig. 1. Discharge tube.

20 mm in diameter. The cathode is a tungsten wire, 1 mm in diameter, positioned in the axis of the cylinder. All the system is enclosed in a glass envelope.

In agreement with previously reported preliminary results (Toupance *et al.*, 1971) all our experiments have been performed under conditions which give a significant synthesis yield simultaneously for many compounds. The pressure in the reactor was maintained at 20 torr in spite of the continuous flow of gases. The residence

time of the mixture in the discharge was 3 s and the discharge current was 100 mA. According to the composition of the initial mixtures, the potential drop varied between 450 and 550 V.

Samples of gaseous effluents have been taken directly at the exit of the reactor and submitted to infrared and gas chromatographic analyses without any chemical treatment. Gas chromatographic samples have been recompressed to 1 atmosphere by a very clean pneumatic system in order to increase sensitivity. Gas chromatographic analysis was performed by using a 3 m × 2 mm i.d. stainless steel column packed with Porapak Q, 80–100 mesh (105°C – He 30 ml/min – T.C. detector). A detailed description of the experimental system and of the analytical procedure and a discussion of the identifications is reported elsewhere (Toupance, 1973).

An attempt to detect the formation of amines was made by using a 3 m × 2 mm i.d. stainless steel column packed with Chromosorb 103. Because no satisfactory resolution between amines, hydrocarbons, and nitriles was found, the search for amines has not been pursued at this time.

### 3. Results

In a first step, pure methane was subjected to the discharge. Among the compounds formed (Figure 2) hydrogen, ethane, ethylene, acetylene, propane, propene, propyne, and isobutane have been identified. Butane and isobutene have been identified but they have not been resolved from other hydrocarbons containing 4 carbon atoms. It can be seen that the amount of each class of hydrocarbon decreases roughly by

	%	
H <sub>2</sub>	41.	
CH <sub>4</sub>	46.	
C <sub>2</sub> H <sub>6</sub>	4.6	} 10.8
C <sub>2</sub> H <sub>4</sub>	2.2	
C <sub>2</sub> H <sub>2</sub>	4.0	
C <sub>3</sub> H <sub>8</sub>	1.2	} 2.0
C <sub>3</sub> H <sub>6</sub>	0.6	
C <sub>3</sub> H <sub>4</sub>	0.2	
iso-C <sub>4</sub> H <sub>10</sub>	0.2	} 0.5
n-C <sub>4</sub> H <sub>10</sub> + t-butene 2	0.08	
iso-butene + butene 1 + butadiene	0.2	

Fig. 2. Molar composition of effluents resulting from subjecting pure CH<sub>4</sub> to the discharge.

a factor 5 when the number of carbon atoms in the chain increases by one. Many higher hydrocarbons have been detected, but at very low levels – lower than 0.1% in the total mixture – and they have not been studied. However, the behaviour of these compounds may be predicted, if necessary, from the set of results obtained from the lighter homologous compounds.

Binary mixtures containing  $\text{CH}_4\text{—NH}_3$  and  $\text{CH}_4\text{—N}_2$  have been made containing various combinations of pure methane and pure ammonia or nitrogen. Figures 3a to 3f give the composition of the effluents as a function of the composition of the initial mixture for the system  $\text{CH}_4\text{—NH}_3$ .

Figure 3a shows that  $\text{CH}_4$  and  $\text{NH}_3$  are similarly decomposed in the discharge. However, the slopes of the curves corresponding to  $\text{NH}_3$  and  $\text{CH}_4$  show that ammonia is more stable in low ammonia-containing mixtures than methane in low methane-containing mixtures. A large amount of hydrogen is always formed while nitrogen always appears to be present in relatively low amounts.

Figure 3b shows the synthesis of the two-carbon containing hydrocarbons. It should be noted that there is approximately twice as much  $\text{C}_2\text{H}_2$  formed as  $\text{C}_2\text{H}_4$ ,

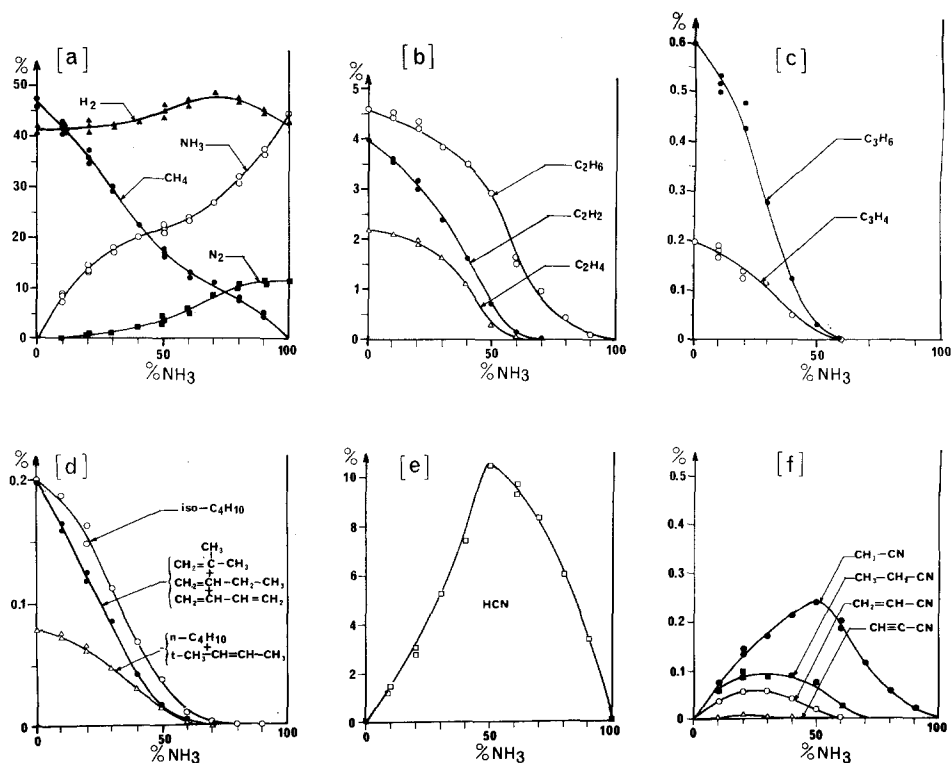


Fig. 3. Molar ratio of several compounds in effluents resulting from subjecting  $\text{CH}_4\text{—NH}_3$  mixtures to the discharge, as a function of the  $\text{NH}_3$  percentage in initial mixtures. 3a,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{N}_2$ ; 3b,  $\text{C}_2$  hydrocarbons; 3c,  $\text{C}_3$  hydrocarbons; 3d,  $\text{C}_4$  hydrocarbons; 3e,  $\text{HCN}$ ; 3f, several nitriles.

and that the amount of these unsaturated compounds decreases rapidly with increasing amount of ammonia in the initial mixture. Their concentration becomes very low when the  $\text{NH}_3$  percentage is higher than 70%. The same behaviour is observed in Figure 3c for the three-carbon containing hydrocarbons. Propane has not been represented because of its interference with HCN on gas chromatograms. In Figure 3d a decrease in the amount of the unsaturated four-carbon containing hydrocarbons can also be observed; the decrease is faster than for the saturated hydrocarbons. Two of the curves represent the area of gas chromatographic peaks corresponding to several unresolved compounds.

Figure 3e represents the synthesis of HCN in  $\text{CH}_4$ — $\text{NH}_3$  mixtures. The maximum amount obtained under our standard experimental conditions is about 10% of the effluent mixture. By increasing the discharge current and the residence time, a higher amount of HCN can be obtained, reaching 25%. The yield of HCN, calculated from  $\text{CH}_4$ , is 30% in an equimolecular  $\text{CH}_4$ — $\text{NH}_3$  mixture and under our standard conditions.

Figure 3f represents the synthesis of several nitriles. The maximum concentration is about 0.2% of the effluent gases. For acetonitrile, this maximum is reached with an equimolecular mixture, and for the other compounds with mixtures containing 20 to 30% ammonia. Cyanoacetylene has been detected only with a 20%  $\text{NH}_3$  mixture and at a very low concentration.

The shape of the curves suggests a mechanism of synthesis in which CN radicals react with a previously formed hydrocarbon. Such an hypothesis has been already proposed for HCN synthesis from  $\text{CH}_4$ — $\text{NH}_3$  mixtures submitted to the action of radiofrequency waves (Topouzkhanian *et al.*, 1967).

The results obtained from  $\text{CH}_4$ — $\text{N}_2$  mixtures are represented on Figures 4a to 4g. As shown on Figure 4a, important differences between  $\text{CH}_4$ — $\text{NH}_3$  and  $\text{CH}_4$ — $\text{N}_2$  mixtures appear for initial methane-poor mixtures. The amount of hydrogen is here continuously decreasing while it is roughly constant, around 45%, in  $\text{CH}_4$ + $\text{NH}_3$  mixtures. The amount of methane in effluent mixtures decreases at the beginning approximately as it does in  $\text{CH}_4$ — $\text{NH}_3$  mixtures, but for initial mixtures, poor in methane, the slopes of the curves are quite different. The amount of remaining methane is here much lower, being a few percent in the range of 70–90%  $\text{N}_2$ , than it is in homologous  $\text{CH}_4$ — $\text{NH}_3$  mixtures. It should be noted that ammonia is always formed in low proportions, not more than 4%, even when both nitrogen and hydrogen are present in effluents in significant concentrations.

Figures 4b to 4d show the results for several hydrocarbons products. It can be seen that unsaturated hydrocarbons are synthesized here in noticeable amounts even from initial mixtures poor in methane. In homologous  $\text{CH}_4$ — $\text{NH}_3$  mixtures these are not detected and they appear only when the initial amount of methane is higher than 40%. This behaviour may be related to the amount of free hydrogen present in the effluent mixtures.

Figure 4e shows that the maximum amount of hydrogen cyanide formed is around 10%, but this maximum is moved from 50% in the case of a  $\text{CH}_4$ — $\text{NH}_3$  mixture

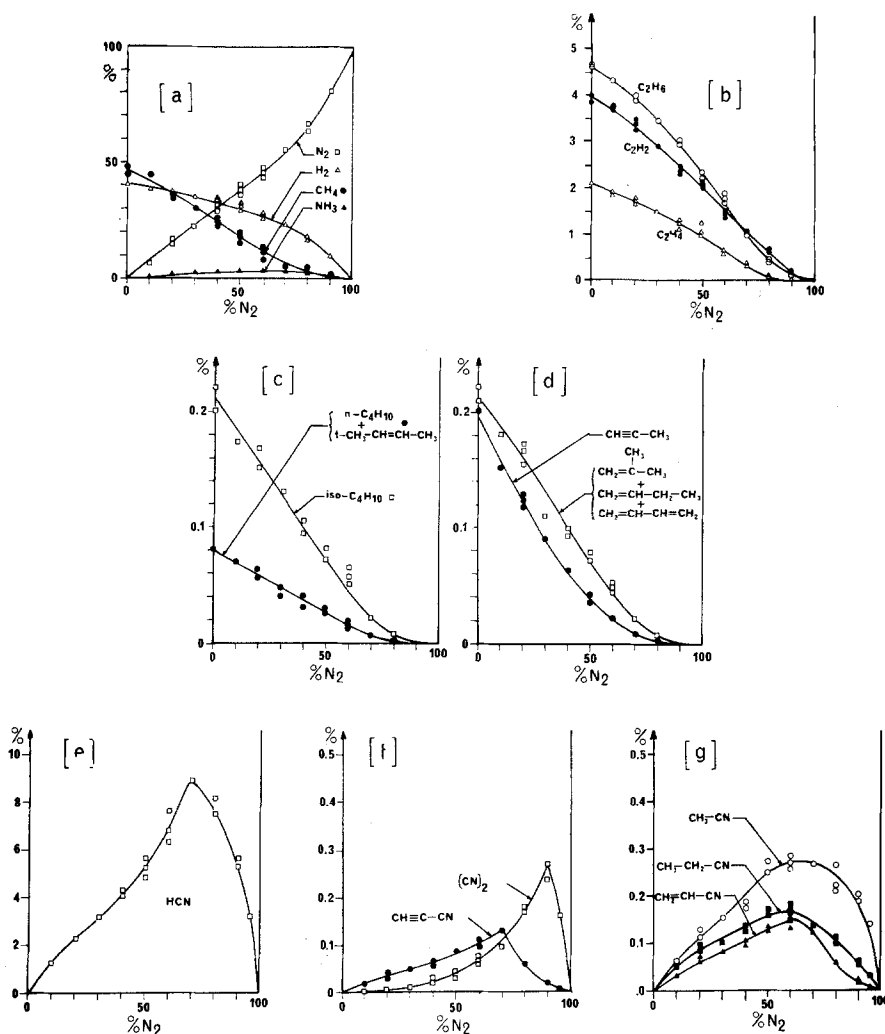


Fig. 4. Molar ratio of several compounds in effluents resulting from subjecting  $CH_4-N_2$  mixtures to the discharge, as a function of the  $N_2$  percentage in initial mixtures. 4a,  $N_2$ ,  $CH_4$ ,  $H_2$  and  $NH_3$ ; 4b,  $C_2$  hydrocarbons; 4c and 4d, several  $C_3$  and  $C_4$  hydrocarbons; 4e,  $HCN$ ; 4f, cyanogen and cyanoacetylene; 4g, several other nitriles.

to 70% in the present case of a  $CH_4-N_2$  mixture. This result has been confirmed by many control experiments.

In Figures 4f and 4g, the formation of several nitrogen-containing compounds is presented. The synthesis of cyanogen and of noticeable amounts of cyanoacetylene should be noted. Contrary to homologous results obtained from  $CH_4-NH_3$  atmospheres (Figure 3f) the amount of all these compounds is higher in atmospheres containing large amounts of nitrogen. The maximum amount of formation of cy-

anogen and cyanoacetylene is reached respectively for 90 and 70%  $N_2$ . For other nitriles, the maximum synthesis is reached at about 60%  $N_2$ .

The synthesis of nitrogen-containing compounds from  $CH_4-N_2$  atmospheres may occur through complex chain reaction involving atomic nitrogen formed in the discharge (Blanton *et al.*, 1966; Safrany and Jaster, 1968). However, we have not yet found a satisfactory explanation for the synthesis of all the compounds.

In order to understand the action of hydrogen during these syntheses, hydrogen has been added to an initial  $CH_4-N_2$  mixture of fixed composition. It has been found that the amount of saturated compounds decreases more slowly than could be predicted from the diluting action of hydrogen. In contrast, the amount of cyanogen and unsaturated compounds is lowered.

As previously indicated, amines have not been systematically analysed. However, if these compounds are synthesized under our conditions, several results show that they are never formed at a level higher than 0.01%.

#### 4. Discussion

Ammonia has been the most regular source of nitrogen used in prebiotic experiments and many interesting results have been obtained. Several experiments also have been carried out using  $N_2$ . In order to complete these results and to unravel the prebiological pathways, many authors have suggested that several precursors may have played a determining role. Among them, HCN has been most frequently invoked but cyanoacetylene or cyanogen may act as key intermediates in the synthesis of pyrimidines, purines, and in phosphorylation reactions (Miller, 1957; Lohrmann and Orgel, 1968; Degani and Halmann, 1971).

New data which have been reported here show that pathways involving cyanoacetylene or cyanogen are most improbable in  $CH_4-NH_3$  containing atmospheres. On the contrary, these two compounds may be considered in atmospheres containing a large amount of free nitrogen and a low amount of hydrogen with respect to the amount of methane. Fortunately, this condition corresponds to the present ideas about the nitrogen state in the primitive atmosphere (Bada and Miller, 1968).

The admixtures free of water vapor we have considered in this report are appropriate models of the bulk of the primitive atmosphere since the water percentage decreases rapidly with altitude. On the contrary, in the lower atmosphere, the presence of noticeable amounts of water should be taken into account.

Studies are now in progress in this laboratory in order to establish the role of water vapor in  $CH_4-NH_3-H_2O$  and  $CH_4-N_2-H_2O$  atmospheres. However, important deviations from results reported in this paper are not expected because additional results obtained respectively from  $CH_4-H_2O$ ,  $CO_2-H_2O$ ,  $CO_2-N_2-H_2O$  and  $CO_2-N_2-H_2-H_2O$  mixtures (Toupance, 1973) have shown that water vapor is a very stable compound which does not introduce any important modification in the evolution of mixtures under investigation.

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