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Cold plasma induced chemical reactions. Implications for molecular evolution

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Abstract

The main aspects of the chemical origins of life research concern the synthesis of so called prebiotic compounds, such as amino acids, purine and pirimidine bases, sugars, etc., and the subsequent steps of their condensation up to proteins and nucleic acids. However, most studies are frequently dedicated to the synthesis of individual compounds, ignoring the complexity of the medium in which they evolved. Cold plasma laboratory simulations corroborated with thermodynamic calculations and space observations are presented.

Introduction

One of the biggest challenge for the human intellect is represented by the origin of life on the Earth. The problem is very old, but its theoretical basis was set up in the middle of this century with the pioneering work of Stanley L. Miller and Harold Urrey in 1953 [1]. Since then many laboratories reported the synthesis of the most building blocks of life. In spite of the recent advances in this field of study there are also many problems which still wait for solving. The first problem is that of the localization, both in space and time, of the origins of life framework. If in the beginnings the Earth was regarded as very serious candidate for appearance of life, because of it's supposed reduced atmosphere, now many supporters of a chemical origin of life tend to place the life's origin, or at least of the compounds needed for it, somewhere in the space. To this result contributed equally the discovery by means of radioastronomy of the whole inventory of the basic compounds needed for prebiotic synthesis and the fact that now is agreed that Earth primeval atmosphere was more oxidized than it was supposed, the organic synthesis in these conditions being almost impossible. However this still represents only a hypotheses.

The work that was done have revealed the basic pathways for prebiotic compounds. A schematic overview of key pathways is presented in Figure 1.

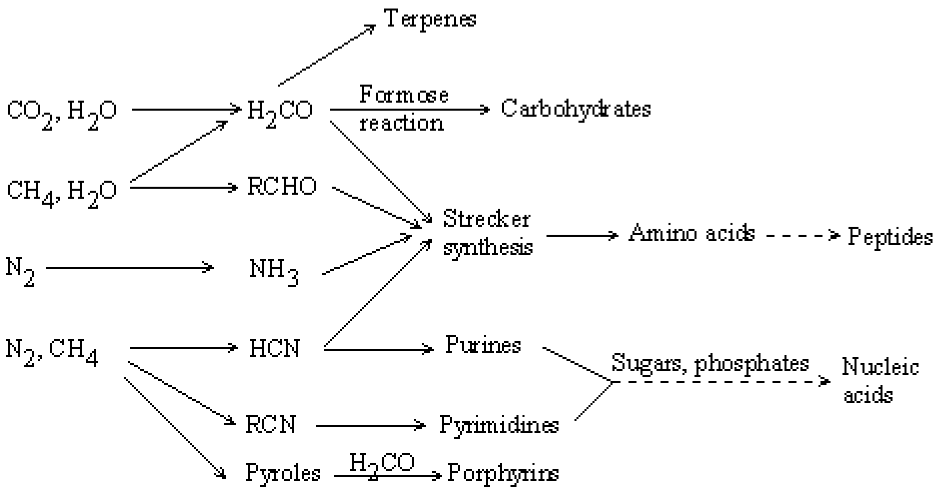


Figure 1. Schematic overview of the pathways involved in the prebiotic synthesis

From this presentation result that the whole inventory of small organic compounds existing in the living world can be derived from a few small inorganic compounds, such as: water, ammonia, hydrogen cyanide and formaldehyde. It is worth noting that these compounds are among the most abundant compounds existing in the cosmic space, after hydrogen and helium [2].

Results and Discussion

Starting from assuming a reduced environment we carried out some chemical synthesis using cold plasma as an energy source. In these experiments were used different types of gaseous mixtures exposed to plasma followed by trapping the resulted mixtures on cold surfaces obtained by freezing of solutions containing different salts. The results were published in some publications [3], [4]. The installation is presented in figure 2.

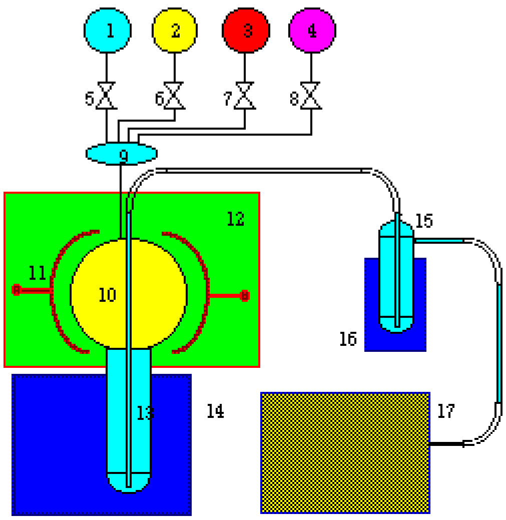


Figure 2. The installation for cold plasma synthesis. 1,2,3,4 - gas cylinders; 5,6,7,8 - valves; 9 - mixing vessel; 10 - plasma reactor; 11 - capacitive electrodes; 12 - RF plasma generator; 13 - cylindrical reactor; 14 - ultracryostat; 15 - liquid N2 cooled trap; 16 - cryostat; 17 - vacuum pump.

This kind of experiments consists in a two stages synthesis: a gas phase one, corresponding to the discharge region, and occurring at the interface with the solid matrix. In the first stage are produced the active species as the result of the interaction of the input mixture with electric field provided by the electrodes. The result is a very complex mixture containing active species (electrons, ions, radicals, photons) and excited molecules, that subsequently react resulting in molecular species that can act as precursors of prebiotic molecules. In order to have an image of this complex chemistry we applied the method of estimation of thermodynamic equilibrium compositions (method of White, Johnson and Dantzig). The distribution of molecular species at chemical equilibrium is independent of the specific reaction by which the equilibrium is reached, the only requiring being the existence of at least one reversible reaction path for the formation of each compound present at equilibrium.

This method, even though it assumes the chemical equilibrium -- a state that is not attained - has proved to be a useful tool in investigating the systems in so called "metastable equilibrium" stage. We applied this method to various systems at different temperatures and pressures. The composition was held constant and correspond to the composition of the system investigated experimentally (CH4:NH3:H2O=3:1:1). The results are presented graphically in the following figures.

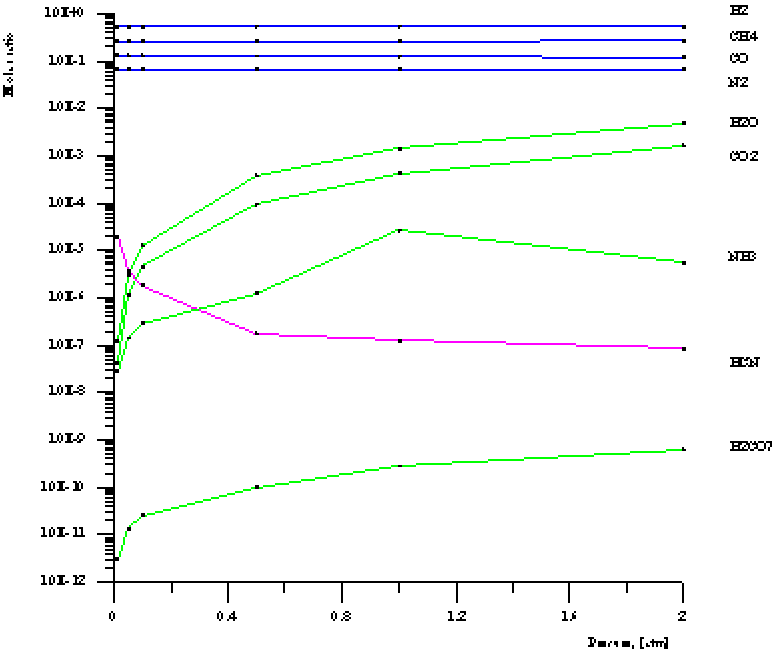


Figure 3a. Dependence of composition of selected species - pressure. The colors on the graphic are according to the evolutionary trend (incresed, decreased or constant molar ratio)

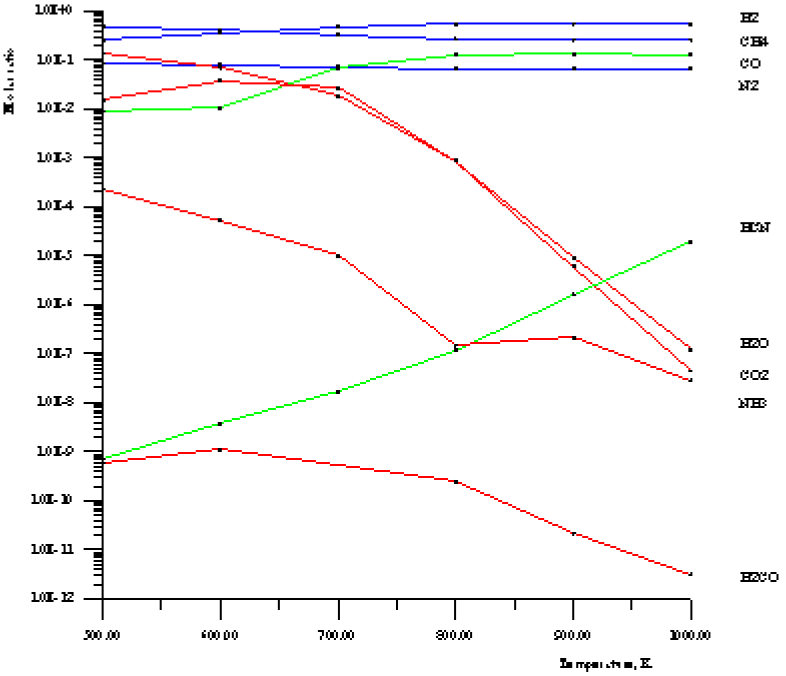


Figure 3b. Dependence of composition of selected species - temperature

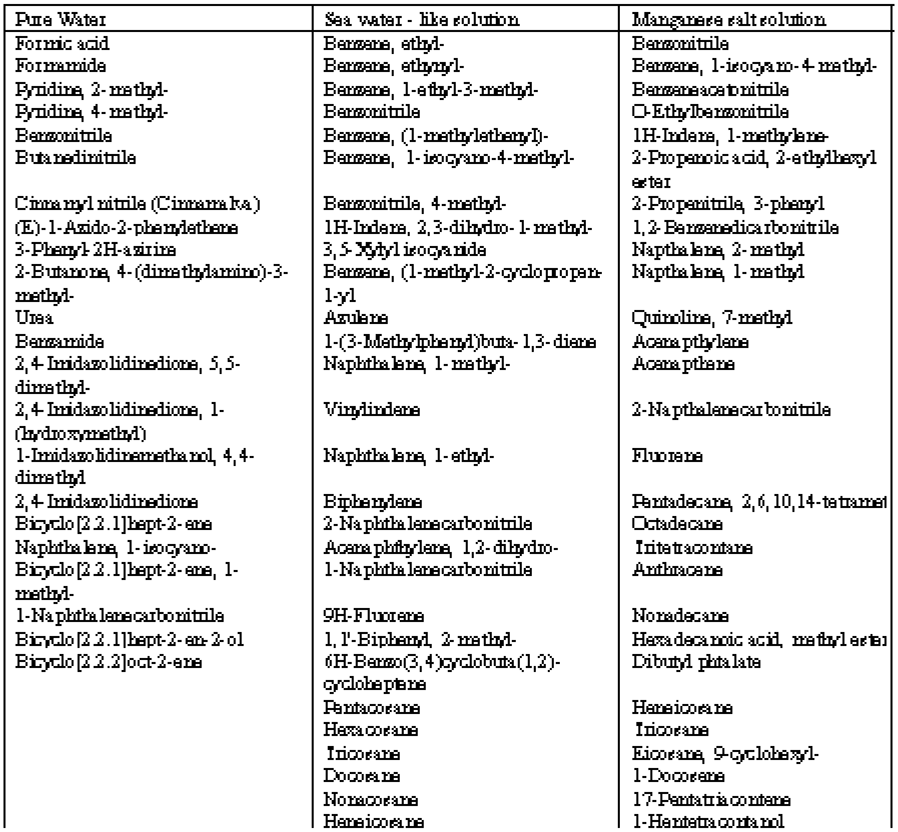
As can be observed from the graphics the distribution of the selected compounds (the most abundant from an extended database) is very close of that observed for the cosmic space. Since the most important precursor, as one can infer from Figure 1, seem to be the hydrogen cyanide, the systems evolving at low pressures have a greater evolutionary potential.

Starting from an open system (CO2 or CH4 / NH3 / H2O), our simulative experiments were carried out in a plasma installation (Figure 2) joining a spherical RF plasma reactor (10) and a cylindrical cooling part (13) for species recombination in the afterglow zone. Experiments were developed with ice deposited on the inner surface of the cylindrical part (13). The ultracryostat (14) maintains the temperature of the cylindrical flask at -60C.

The parameters of the plasma syntheses were: pressure during the synthesis, 460 - 660 Pa; temperature of cooling zone, 113 K; time, 4 hours, and dissipated power, 4.8 kW. Water was introduced in different ways: 500 ml initially (ice from artificial "sea water" on the cylindrical surface of the reactor) and during the synthesis 5 mg/s water vapor in the atmosphere for RF plasma discharge. The feed mixtures were: initial CO2 or CH4 partial pressure, 200 Pa; initial NH3 partial pressure, 66 Pa; initial water partial pressure, 66 Pa. Artificial "sea water" was prepared from salts (p.a. purity grade) in order to achieve the main marine ionic composition: NaCl 25.082 g/l, CaCl 2 1.360 g/l, MgSO4 .7H2O 7.093 g/l, Na2HPO4.12H2O 1.081 g/l, KCl 1.070 g/l and MgCl2 2.078 g/l. Other experiments used a manganese salt (MnCl2).

Before the reaction, the installation was cleaned with air (direct valve injection) and H2 (from cylinder (4) through a needle valve (8)) plasma. Known amounts of carbon dioxide, ammonia and water were introduced into the mixing chamber (9) through needle valves (5-7). The mixture obtained was continuously admitted into the spherical part (10) of the apparatus, where an electric discharge was provided by (12) a high-frequency generator (5 kW and 13.6 MHz) by means of two external silver-plated electrodes (11). The vacuum (460 - 660 Pa) and open system condition was ensured by a pump (17) protected by a N2 cooled trap (15). The volatile compounds from a reactive plasma synthesis are captured in trap (15) cooled with the cryostat (16). The active species formed in the cold plasma were adsorbed on the ice deposited previously (from "sea water") on the wall and at the bottom of the cylindrical flask (13), cooled to -60C with ethanol and recirculated locally through a cooling system (17).

It was observed (Figure 4) that the final reaction mixture was different, not only based on the initial gaseous mixtures but also on the solid matrix salt content (at the same gaseous input).



Pure Water	Sea water - like solution	Manganese salt solution
Formic acid	Benzene, ethyl-	Benzonitrile
Formamide	Benzene, ethynyl-	Benzene, 1-isocyano-4-methyl-
Pyridine, 2-methyl-	Benzene, 1-ethyl-3-methyl-	Benzeneacetonitrile
Pyridine, 4-methyl-	Benzonitrile	O-Ethylbenzonitrile
Benzonitrile	Benzene, (1-methylethenyl)-	1H-Indene, 1-methylene-
Butanedinitrile	Benzene, 1-isocyano-4-methyl-	2-Propenoic acid, 2-ethylhexyl ester
Cinnamyl nitrile (Cinnamalva)	Benzonitrile, 4-methyl-	2-Propenitrile, 3-phenyl
(E)-1-Azido-2-phenylethene	1H-Indene, 2,3-dihydro-1-methyl-	1,2-Benzenedicarbonitrile
3-Phenyl-2H-azirine	3,5-Xylyl isocyanide	Napthalene, 2-methyl
2-Butanone, 4-(dimethylamino)-3-methyl-	Benzene, (1-methyl-2-cyclopropen-1-yl	Napthalene, 1-methyl
Urea	Azulene	Quinoline, 7-methyl
Benzamide	1-(3-Methylphenyl)buta-1,3-diene	Acenaptylene
2,4-Imidazolidinedione, 5,5-dimethyl-	Naphthalene, 1-methyl-	Acenaptene
2,4-Imidazolidinedione, 1-(hydroxymethyl)	Vinylindene	2-Napthalenecarbonitrile
1-Imidazolidinemethanol, 4,4-dimethyl	Naphthalene, 1-ethyl-	Fluorene
2,4-Imidazolidinedione	Biphenylene	Pentadecane, 2,6,10,14-tetramet
Bicyclo[2.2.1]hept-2-ene	2-Naphthalenecarbonitrile	Octadecane
Naphthalene, 1-isocyano-	Acenaphthylene, 1,2-dihydro-	Tritetracontane
Bicyclo[2.2.1]hept-2-ene, 1-methyl-	1-Naphthalenecarbonitrile	Anthracene
1-Naphthalenecarbonitrile	9H-Fluorene	Nonadecane
Bicyclo[2.2.1]hept-2-en-2-ol	1,1'-Biphenyl, 2-methyl-	Hexadecanoic acid, methyl ester
Bicyclo[2.2.2]oct-2-ene	6H-Benzo(3,4)cyclobuta(1,2)-cycloheptene	Dibutyl phtalate
	Pentacosane	Heneicosane
	Hexacosane	Tricosane
	Tricosane	Eicosane, 9-cyclohexyl-
	Docosane	1-Docosene
	Nonacosane	17-Pentatriacontene
	Heneicosane	1-Hentetracontanol

Figure 4. The results of different plasma simulation (partial listing)

The significance of these results is increased taking into account the great diversity of compounds which can be obtained in particular experiments simulating a practically infinite number of microenvironments. The compounds previously listed add to a number of other compounds, which have also been reported and that have an enormous prebiotic potential (amino acids, nucleic acid bases, etc.). It is worth mentioning that the class distributions of the compounds (aromatic, short and long chain aliphatic, etc.) resemble the distribution pattern resulted from the analysis of some meteoritic fragments [5], assumed as the result of Fischer-Tropsch type reactions.

Conclusions

The experimental results point to a more important role of inorganic cations and anions in evolutive processes.

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