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DIAGNOSTICS OF NITROGEN-METHANE ATMOSPHERIC GLOW DISCHARGE USED FOR A MIMIC OF PREBIOTIC ATMOSPHERE

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Abstract. The exploration of planetary atmosphere is being advanced by the exciting results of the Cassin-Huygens mission to Titan. The complex chemistry revealed in such atmospheres leading to the synthesis of bigger molecules is providing new insights into our understanding of how life on Earth developed. This work extends our previous investigation of nitrogen-methane (N_2-CH_4) atmospheric glow discharge for simulation chemical processes in prebiotic atmospheres. In presented experiments 2 % of water vapor were addet to nitrogen-methane gas mixture. Exhaust products of discharge in this gas mixture were in-situ analysed by Fourier Transform Infra Red spectroscopy (FTIR). The major products identified in spectra were: hydrogen cyanide, acetylene and acetonitrile.

Keywords: prebiotic atmosphere, Fourier Transform Infra Red spectroscopy, glow discharge.

1. Introduction

More than 60 yers ago, S. Miller and H. Urey [1], in their exciting work, demonstrated the synthesis of several amino acids from a mixture of reducing gases (CH_4, NH_3, H_2O, and H_2) treated with electric discharge. The following explorations showed that a broad array of amino acids could be synthesized, but there was no evidence that all of the fundamental molecules of the RNA genetic code could be produced alongside others in this type of experiment [2, 3]. Recently it was also referred to a positive result on qualitative detection of RNA nucleobases and manifold amino acids from tholines created in a N_2, CH_4, CO mixture [4]. This experiment simulated the atmosphere of Titan by electric discharge. Such experimental results as well as theoretical expectations [5] show that reduced, relatively reactive atmospheres are likely to be more efficient for the synthesis of biomolecules [6]. The gliding arc configuration of atmospheric pressure discharge has been shown to be a good mimic of processes in the prebiotic atmospheres [7] being used to replicate physical and chemical conditions on Titan. It is the only lunar body with significant quantities of methane (CH_4) and nitrogen (N_2) in its atmosphere [8, 9]. The chemical composition of the Titan's atmosphere is considered to be similar to the atmosphere of early Earth and it is favorable for formation of complex molecules containing C, N and H. The solar ultraviolet radiation and magnetospheric electrons are responsible for the generation of primary radicals and other neutral species, which initiate chains of chemical reactions that finally result in the formation of various organic molecules in the Titan atmosphere. This makes Titan as planetary-scale laboratory for the synthesis of complex organic molecules [10].The composition of early Earth atmosphere was deeply discussed in many studies [11–13].

The present work is focused on the experimental study of gaseous products produced in the atmospheric pressure glow discharge fed by N_2, CH_4 gas mixtures with CH_4 concentrations in the range from 1 % to 5 % and admixture of 2 % water vapor (H_2O). The atmospheric DC glow discharge is a source of electrons, ions and neutral radicals. All these species initiate a complex chemical processes under laboratory conditions, which are similar to the processes which may occur in the prebiotic atmosphere. The neutral products generated in the discharge were identified and quantified by the means of the Fourier-Transform-Infra-Red spectroscopy (FTIR). In more detail the influence of the H_2O admixture on production of HCN (the major neutral product) and on the formation of NH_3 has been studied.

2. Experimental setup

The experimental setup schematic drawing is shown in Figure 1. The special high vacuum stainless steel reactor was constructed for our experiments to prevent any oxygen contamination during the experiments. Nitrogen and methane flows were automatically controlled by Bronkhorst controllers. The measurements were carried out at total gas flows 100 sccm at atmospheric pressure and laboratory temperature. The discharge electrode system had the standard configuration of the gliding arc discharge. The discharge was formed in the stable abnormal glow regime, and

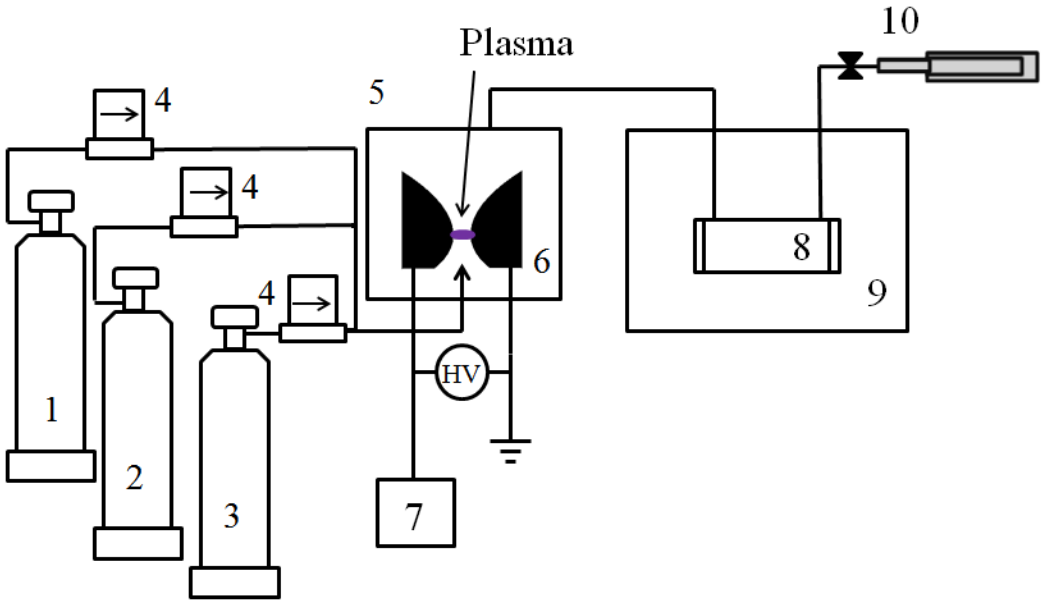

Figure 1. Experimental setup. 1- storage bottle of nitrogen, 2- storage bottle of methane, 3- storage bottle of carbon dioxide, 4- Bronkhorst controllers, 5- reactor body, 6- electrode system, 7- oscilloscope, 8- IR gas cell, 9- FTIR spectrometer, 10- exhaust.

plasma occurred between the electrodes at their shortest distance of 2 mm in the form of a plasma channel of 1 mm in its diameter. The reactor chamber volume was 0.5 l. The discharge was supplied by a DC stabilized HV source. Discharge breakdown voltage was 1500 V, a stable plasma channel was operating at 400 V at current in range 15 mA to 40 mA during all presented experiments. The measurements were performed for different N_2:CH_4 ratios in the range from 1 % to 5 % of methane in nitrogen (both gases having quoted purities of 99.995 %). There was connected bottle gas washing with a high purity water just before the entrance to the reactor. The amount of added water vapour was estimated at 2 % in gas mixture in all performed experiments. The exhaust gas was analyzed in-situ by FTIR spectroscopy using IR cell with total length of 15 cm.

The electrode system is made of stainless steel and it is necessary to clean it after each set of experiments. The deposit created during discharge operation is shown in Figure 2 . Before starting the experiments, the discharge chamber was pumped down to 1 Pa for 1 h and then was filled with the investigated gas mixture up to the pressure of 101 kPa. Atmospheric pressure during the experiments was maintained by a slight pumping through the needle valve.

Figure 2. Photos of the electrodes with deposited layers.

3. Results and Discussion

A typical FTIR spectrum showing the products formed in the nitrogen discharge fed by 4 % of CH_4 and 2 % of H_2O is shown in Figure 3. Similar spectra were also observed for other N_2:CH_4:H_2O ratios. Hydrogen cyanide (HCN) was found to be the most abundant product at wavenumbers of 1430 cm^{-1} and of

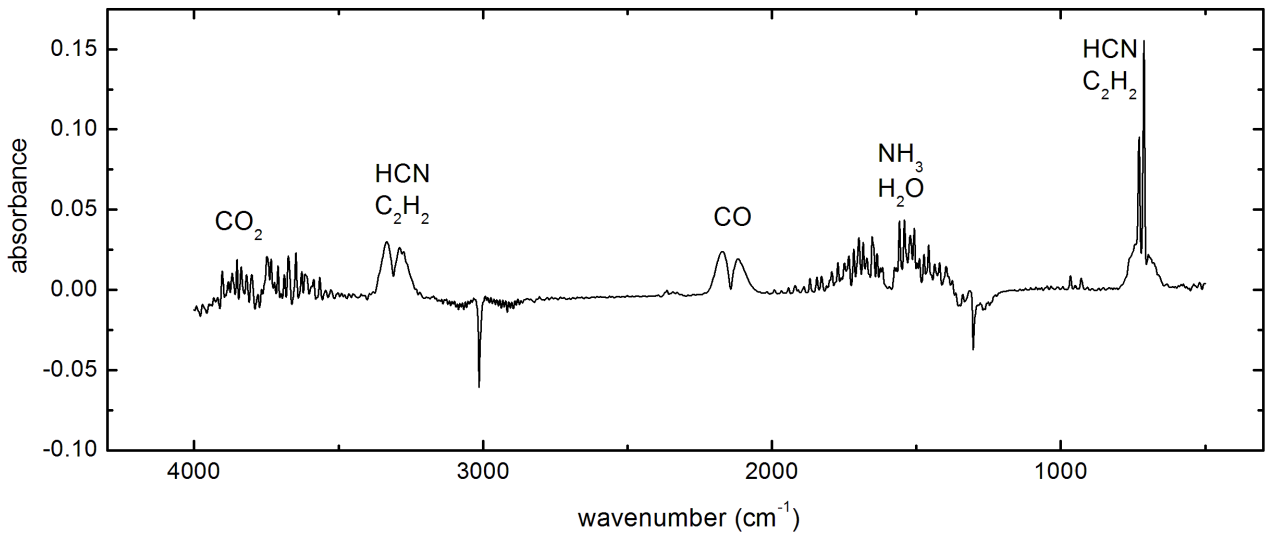

Figure 3. FTIR spectrum recorded in mixture N_2:CH_4 = 96:4 with 2 % H_2O vapor addition at flow rate of 100 sccm and discharge current of 20 mA.

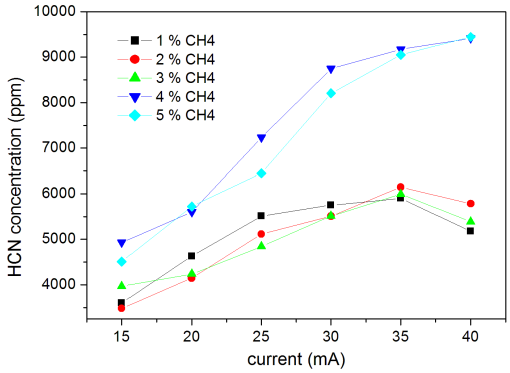

Figure 4. The dependence of hydrogen cyanide concentration on discharge current for different initial concentration of methane.

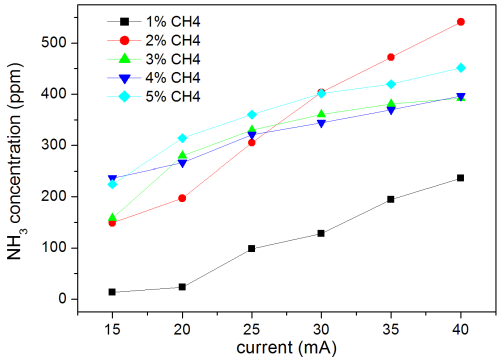

Figure 5. The dependence of ammonia concentration on discharge current for different initial concentration of methane and carbon dioxide.

720 cm^{-1}. This is in agreement with [7]. Ammonia (NH_3), which was identified at 966 cm^{-1}, was also detected in our previous experiments. The other major products were acetylene (C_2H_2) as well as carbon monoxide (CO). These products were recognized in all investigated gas mixtures. The products concentrations depend on the composition of the gas mixtures. Quantitative analysis of selected hydrocarbons were done in dependence on the methane concentration. The absorbance was calculated as an area under the recorded peaks and the concentations of selected products were then calculated. Figures 4 and 5 show dependences of HCN (1430 cm^{-1}) and NH_3 (966 cm^{-1}) concentrations formed under different experimental conditions. The increase of the initial discharge current from 15 mA to 40 mA leads to increase in the product yield of these compounds.

4. Conclusions

The gaseous products formed in the atmospheric glow discharge fed by different mixtures of nitrogen, methane and water were determined by in situ FTIR analysis. The discharge was operated in the flowing regime at different discharge currents at laboratory temperature. An in-situ FTIR technique for the exhaust gas phase sampling was successfully used for chemical analysis to deduce the gas composition in the N_2:CH_4:CO_2 reactive gas mixture mimics of Titan's atmosphere. Various hydrocarbons were observed in all experiments. HCN was identified as the major gas phase product in all of measurements. Others minor products detected were C_2H_2, NH_3, CO_2, CO. These results are consistent with the Titan's atmospheric composition because the same compounds were detected during the Cassini-Huygens space mission. CO could have an effect on the atmospheric reactivity

of Titan. The formation of organic molecules incorporating oxygen in gases could occur in the upper atmosphere of Titan where the dissociations of N_2 and CO_2 by VUV photons and magnetospheric electrons are possible. This fact clearly demonstrates that laboratory experiments can be used for prediction of both the presence and possible concentrations of compounds which have not been detected, yet. These simple organics should be tracers of the chemical groups constituting the dusty products.

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