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GC-MS AND GC-FID ANALYSIS OF PRODUCTS FROM GLOW DISCHARGE IN N_2 + CH_4 MIXTURE

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Abstract. This work extends our previous investigation of nitrogen-methane atmospheric glow discharge for the simulation of chemical processes in prebiotic atmospheres. Beside the volume chemical reactions also heterogeneous chemical reactions on surfaces of solid state bodies can be important. So in presented experiments the electrodes with different shapes and different surface areas were used. Exhaust products of discharge in this gas mixture were analyzed by Gas Chromatography - Mass Spectrometry (GC-MS) and Gas Chromatography - Flame Ionization Detector (GC-FID). The major products identified in chromatograms were hydrogen cyanide and acetylene.

Keywords: prebiotic atmosphere, GC-MS, GC-FID, glow discharge.

1. Introduction

The effect of an electric discharge on gas mixtures of methane (CH_4) and nitrogen (N_2) has been shown to result in the synthesis of many different biologically important organic compounds including ammonia. It has been also shown that ammonia can be produced in discharges at atmospheric pressure [1] and it is assumed that ammonia can be created by reactions on surfaces [2]. The electrical discharges are believed to imitate the effect of thunderstorm lightning on chemical processes in prebiotic atmospheres. Indeed the Miller-Urey spark discharge experiments in the early 1950s [3, 4] were the first experimental studies describing results in reducing atmospheres and led to the start of laboratory studies of the origins of prebiotic material on the Earth. The atmospheric pressure glow discharges are of significant interest for a wide range of applications such as pollution control, material processing or surface treatment. The gliding arc configuration has been shown to be a good mimic of processes in the prebiotic atmospheres being used to replicate physical and chemical processes e.g. on moon Titan. Titan is the largest moon in Saturn's lunar system and the only one with a dense atmosphere, with atmospheric surface pressure of approximately 1.5×10^5 Pa [5]. It is the only lunar body with a significant quantities of CH_4 and N_2 in its atmosphere [6, 7]. The chemical composition of the Titan's atmosphere is favorable for formation of complex molecules containing C, N and H. The solar ultraviolet radiation and electrons from Saturn's magnetosphere 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 [8]. 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%. Also the influence of surface processes was studied, namely two types of electrodes were used. The first ones were electrodes in standard gliding-arc configuration with large surface area. The second ones were the electrodes made of wires.

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 two configurations: i) configuration of the gliding arc discharge (see Figure 1), ii) two wires with diameter of 2 mm. Both types of electrodes were made of copper. The wire electrodes were fixed in one line and the distance of their tips was 2 mm. The discharge was formed in the stable abnormal glow regime, and 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

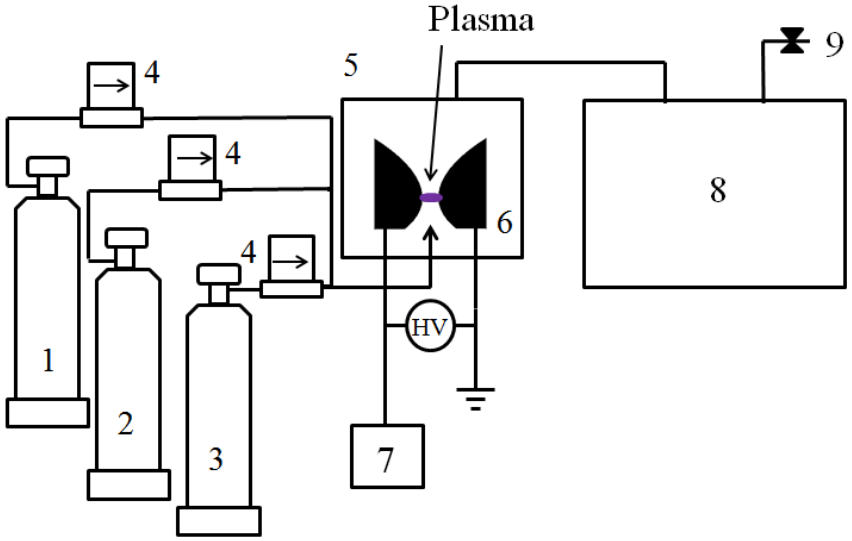

Figure 1. Experimental setup. 1- storage bottle of nitrogen, 2- storage bottle of methane, 3- storage bottle of oxygen, 4- Bronkhorst controllers, 5- reactor body, 6- electrode system, 7- oscilloscope, 8- GC-MS, GC-FID, 9- exhaust.

(both gases having quoted purities of 99.995 %). The exhaust gas was analyzed by GC-MS and GC-FID methods.

Before starting the experiments, the discharge chamber was pumped down by oil rotary vacuum pump 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.

GC-MS analysis was carried out using an Fisions Instruments 8060 gas chromatograph. Separation was performed on a Polar plot Q-HT + 2PT column (25 m length, 0.32 mm internal diameter) using helium flow of 2 sccm as the carrier gas. The GC oven temperature was held for 3.3 min at 50°C and then increased with the step of 15°C min^{-1} to 250°C, whereas the final temperature was held for 3 min.

3. Results

A typical GC-MS chromatogram showing the products formed in the nitrogen discharge fed by 5% of CH_4 is shown in Figure 2. Similar spectra were also observed for other N_2:CH_4 ratios. Hydrogen cyanide (HCN) was found to be the most abundant product at the retention time 9 min. The second major product was acetylene (C_2H_2). Other detected compounds are signed in spectrum. These products were recognized in all investigated gas mixtures, they were also detected in previous experiments [9]. The intensities shown in the following graphs were calculated as the area bellow corresponding peaks. These intensities are proportional to the product concentrations. The dependence of C_2H_2 concentration on CH_4 addition is shown in Figure 3. The C_2H_2 concentration increases with increasing methane concentration as was already observed in previous experiments [9]. The MS and FID detection methods provide the same results. Also there is no significant difference of acetylene concentration between both types of electrodes. So the surface reactions are not important for acetylene creation. The same features were observed for HCN, see Figure 4. The decrease of HCN concentration at 4% of CH_4 is probably caused by carbon (graphite) deposit on the tip of the wire electrodes. This deposit was observed during the experiments and it could changed the discharge properties. The dependencies of C_2H_2 and HCN concentrations on discharge current are shown in Figures 5 and 6. There is no clear increasing dependence of products concentrations on discharge current as in previous study [1]. This is probably caused again by thick graphite deposit which was created on electrode surfaces. Such thick deposit was observed when copper electrodes were used, substantially thinner graphite deposit was observed when the stainless steel electrodes were used [10].

Finally, the influence of oxygen addition to N_2+CH_4 mixture was studied. The oxygen content was changed from 1% to 3%. The water molecules were observed in GC-MS chromatograms in this case, no other oxygen containing molecules were observed. The concentrations of hydrocarbons and nitriles decrease with increasing oxygen content. So the oxygen has opposite influence then carbon dioxide, the addition of carbon dioxide leads to concentration increase of major products [1].

4. Conclusions

The concentrations of major products (acetylene and hydrogen cyanide) from DC glow discharge in nitrogen methane mixture were measured by GC-MS and GC-FID methods. It was found using electrodes with

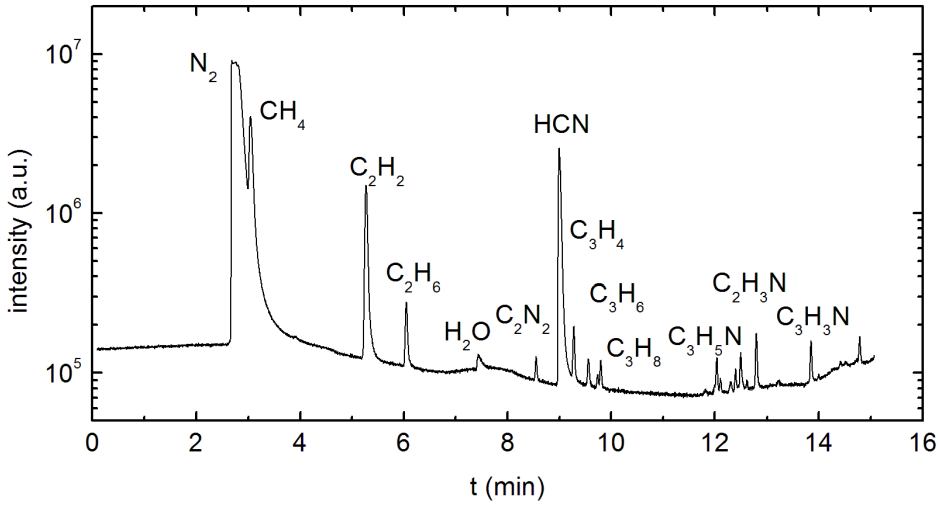

Figure 2. GC-MS spectrum of the gas-phase products from the discharge of 5% of CH_4 in N_2 for discharge current 30 mA.

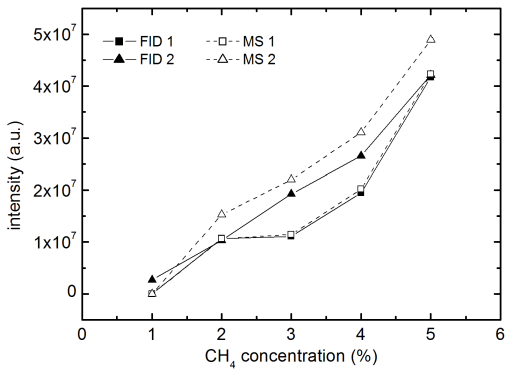

Figure 3. The dependence of C_2H_2 concentration on CH_4 addition. FID 1 and MS 1 are the results from experiments with gliding-arc electrodes configuration, FID 2 and MS 2 are the results from experiments with wire electrodes.

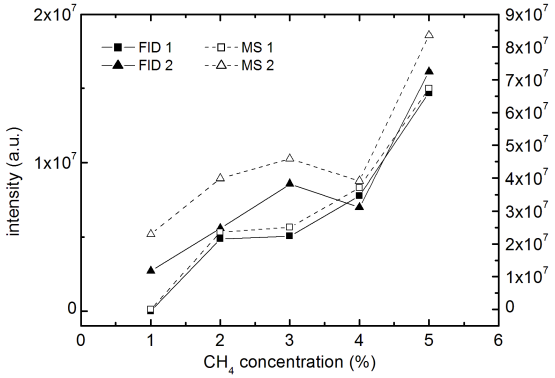

Figure 4. The dependence of HCN concentration on CH_4 addition. FID 1 and MS 1 are the results from experiments with gliding-arc electrodes configuration, FID 2 and MS 2 are the results from experiments with wire electrodes.

different surface area that the surface reactions are not important for productions of these two products. The use of copper as a electrode material leads to large amount of carbon deposited on electrode surfaces.

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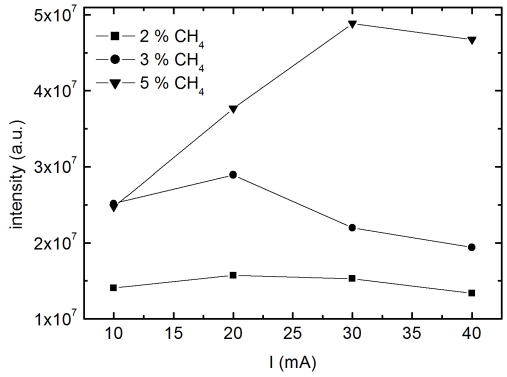

Figure 5. The dependence of C_2H_2 concentration on discharge current. The results are from experiments with gliding-arc electrodes configuration.

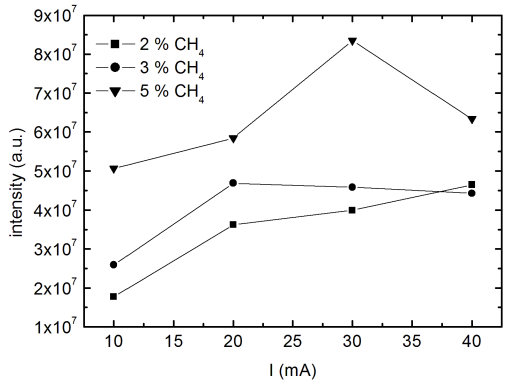

Figure 6. The dependence of HCN concentration on discharge current. The results are from experiments with gliding-arc electrodes configuration.

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