Synthesis of chemical compounds in the gaseous mixture related to Titan atmosphere by glow discharge at the relevant temperature and pressure

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Abstract: Chemical processes initiated by electrical discharges in prebiotic atmospheres like at Titan became a hot topic during the last decade because of extensive discovering of exo-planets. The presented contribution gives the first PTR-TOF measurements of the main compounds formed in the glow discharge in nitrogen-methane gaseous mixture with oxygen traces at temperature of 77 K and atmospheric pressure. The life precursor molecules like formamide were observed in significant amount.

Keywords: Glow discharge, PTR-TOF spectrometry, astro chemistry, life precursors.

1. Introduction

Laboratory mimic studies of processes running in the exo-planetary atmospheres became a hot topic during the last years because many exo-planets were discovered very recently and their number increases very rapidly. Moreover, the successful space missions like Cassini-Huygens bring a huge number of data from the in situ observations that are impossible using the earth techniques [1-3]. The main interest is focused on the search of life traces or life molecular precursors and consequent discovering the possible ways leading to the life origins formation. The majority of studies were carried out in the Titan's atmosphere up to know because there are many in situ available data and its atmosphere seems to be very similar as the Earth's one before the life creation [3-5]. Besides the planetary atmospheric processes initiated by UV and VUV radiation and particles fluxes coming from the space, the electrical discharge phenomena can play an important role in the planetary atmosphere chemistry [6]. Lightning was confirmed in more planetary atmospheres [7, 8]. The planetary scale processes can be simulated by laboratory experiments using various discharges: corona and DBD conditions are similar as the St. Elmo's fire, spark and arc relates to the lightning, and corona and glow conditions are similar to conditions in aurora borealis. Nearly all laboratory studies of Titan atmosphere discharge initiated processes were carried out at ambient temperatures and pressure up to now that are not fully reflecting the real Titan surface conditions. The presented study gives the first results obtained by glow discharge generated in the Titan like atmosphere (nitrogen-methane mixture) in the flowing regime at the liquid nitrogen temperature [5, 9].

2. Experimental

The experiment was carried out in the simple glass reactor (see Fig. 1) equipped by a pair of tungsten rod electrodes (diameter of 1 mm) in the distance of 1 mm for the glow discharge creation. Two sets of experiments were completed. The first one was carried out in the nitrogen-methane mixture (200 + 1 Sccm) at the currents of 10, 20, and 30 mA (corresponding powers of 3.5, 7.0, and 10.5 W) at the atmospheric pressure. Four different mixtures were used for the second part of the experiments: pure nitrogen with flow of 200 Sccm, nitrogen with addition of 5 Sccm of methane and the same mixture enriched by oxygen or CO_2 with flows of 1 Sccm. Pressure in the reactor was kept as atmospheric and the discharge current was kept at 25 mA (corresponding power was 9 W).

The reactor was placed into the Dewar vessel fillable by liquid nitrogen up to level 2 cm above the electrode system. The gas mixture composition was controlled by Bronkhorst MCFs. Used gasses were of the following purities: nitrogen 99.999%, methane 99.95%, oxygen 99.5% and CO_2 of alimentary quality.

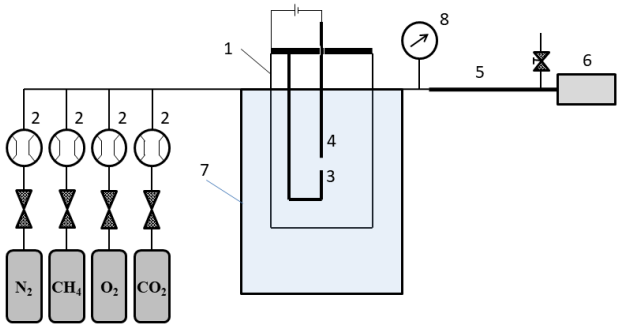

Fig. 1. Scheme of the experimental set up: 1 – Pyrex glass reactor vessel; 2 – mass flow controller; 3 – cathode; 4 – anode; 5 – heated exhaust gas sampling line; 6 – proton transfer reaction time of flight mass spectrometer; 7 – liquid nitrogen vessel; 8 – membrane manometer.

The exhaust gas analysis was examined by proton transfer reaction time of flight (PTR-TOF) mass spectrometry allowing continual in situ complex analysis of the discharge exhaust gas. Advantage of this technique is the immediate response and the simultaneous detection of all compounds with proton affinity higher than proton affinity to water molecules. Thus it is not sensitive to any of the gasses in the reaction mixture. Unfortunately, it is impossible to distinguish isomers. The whole line (made of PTFE and stainless steel) to the PTR-TOF mass spectrometer was heated up to 80 °C to avoid discharge products condensation (on the other hand, it allowed decomposition of various clusters formed by the discharge at low temperature). Experiments were

completed according to the following scheme shown in Table 1.

Table 1. Experimental procedures.

point	EXP 1	EXP 2	Description
1	-300 s	-300 s	start of the reaction mixture flow
2	0 s	0 s	start of the measurement
3	60 s	60 s	the discharge turn on
4	600 s	300 s	start of the reaction vessel cooling
5	1800 s	1200 s	the discharge off
6	2400 s	1500 s	end of the vessel cooling
7	3000 s	2100 s	start of the reactor heating by the hair drier
8	3300 s	2400 s	end of the reactor heating by the hair drier
9	3300 s	2700 s	nitrogen (99.999%) high flow of 5 Slm purge flow on
10	4200 s	3000 s	end of the experiment

Reactor was not opened or cleaned between experiments (it was only flowed by pure nitrogen for times given in Table 1), so some contamination (mainly by some deposited material on electrode surfaces) was possible.

3. Results

Time profiles of concentrations for the selected compounds during the first experimental set are given in Figs. 2-4. Hydrogen cyanide (Fig. 2) and acetonitrile (Fig. 3) are the main compounds formed by the discharge in nitrogen-methane mixtures [10, 11]. Hydrogen cyanide and acetonitrile reach the saturation limit of the current device during the discharge operation and later evaporation of condensed discharge products and thus it is rather complicated to relate them to appropriate kinetic processes. Additionally, the time profile of HCN shows a strong dependence on the applied power. At the lowest one, the simple production in the discharge is visible followed by the concentration decrease during the cooling (due to the trapping on the cold reactor walls) followed by the strong concentration increase during the reactor heating. The profile obtained at the medium power of 7 W shows the more complicated behaviour. The significant concentration decrease is observed during the discharge operation at the ambient temperature. The additional concentration drop is visible just at the beginning of the discharge cooling and later the concentration reaches nearly the same value as at the lowest power up to the discharge switching off. The concentration profile after the reactor heating is nearly the same as at the lowest applied power. The most complicated curve was obtained at the highest power. The behaviour up to the end of the cooling is similar as at the medium power but the first concentration drop starts sooner and it is deeper than before. Also the concentration during the cooling period is about 30% lower than at the medium power. We are supposing that this is due to the higher dissociation degree at the higher applied power and consequent formation of bigger molecules. The dependence after the start of the reactor self-heating shows three huge peaks of the HCN presence. There is no reason for this besides the secondary formation of HCN molecules from some bigger clusters deposited (trapped) on the reactor walls.

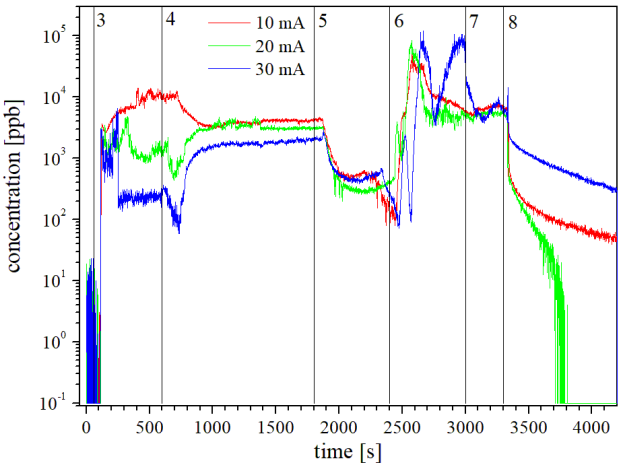

Fig. 2. Concentration of hydrogen cyanide during the first experiment. The vertical lines indicate experimental setting points given in Table 1. Note that saturation limit for the used detection technique is about 60 000 ppb for this compound.

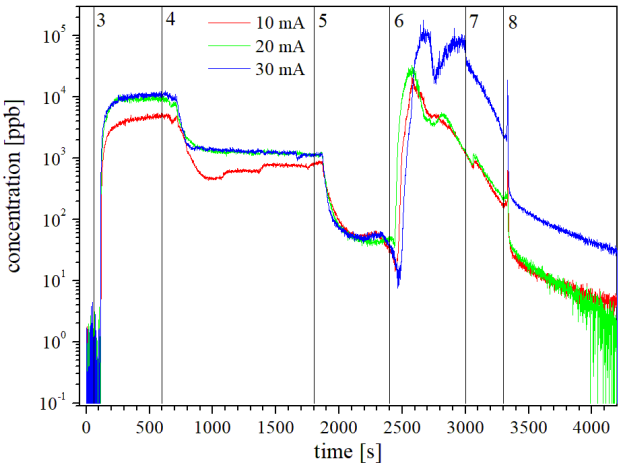

Fig. 3. Concentration of acetonitrile during the first experiment. The vertical lines indicate experimental setting points given in Table 1. Note that saturation limit for the used detection technique is about 60 000 ppb for this compound.

The production of acetonitrile (see Fig. 3) in the discharge is increasing with the applied power but it has probably some saturation limit. No unexpected points like in case of HCN were recorded. The concentration time profile during the heating part of the experiment shows nearly the same dependences for both applied powers with the faster concentration increase in case of the medium power. Two concentration peaks are visible for the highest applied power, similar like in the case of HCN (the concentration drop is at the same time for both compounds).

Besides the main formed compounds, many tens of other species were successfully identified [10, 11]. Interesting among them is the formation of benzene (see Fig. 4) as the simplest aromatic compound. Its formation in the discharge at ambient temperature shows strong power dependence. The significant decrease of benzene concentration is visible at the highest applied power during the discharge operating at the liquid nitrogen temperature. We can suppose two effects. The first one is the better benzene trapping due to the presence of some other molecules trapped on the glass reactor wall (i.e. surface conditions changes). The second one is the formation of some other (probably bigger) molecules at these conditions. This second possibility is more probable because the concentration time dependence during the reactor heating is different from other in the case of the highest applied power. The secondary reactions as described in case of HCN are also probable in case of benzene (see the curve between point 6 and 7). The final enhancement of benzene concentration after the heating switching on is due to its evaporation from walls.

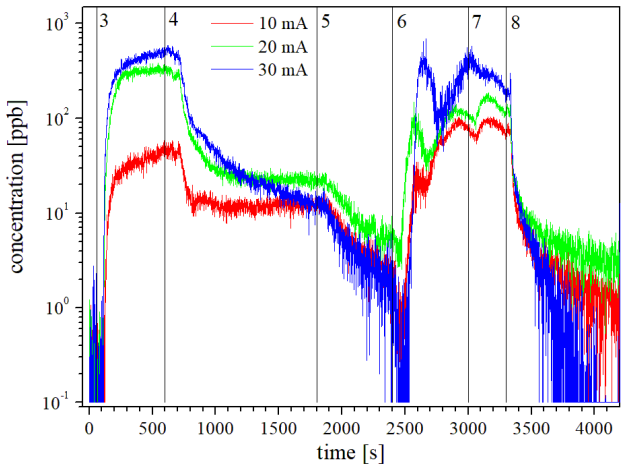

Fig. 4. Concentration of benzene during the first experiment. The vertical lines indicate experimental setting points given in Table 1.

The second part of experiment was devoted to verification of the oxygen containing molecules role in the formation of the same species as above. The formation of molecules not containing oxygen is not so much influenced by presence oxygen impurities, their concentrations are only slightly decreased. As an example, the formation of hydrogen cyanide is shown in Fig. 5. On the other hand, the formamide formation (see Fig. 6) is strongly supported by oxygen presence because this molecule contains oxygen in its structure. It is important to note that formamide is formed by the discharge also in case when no additional oxygen is added into the reaction mixture. That is why even small oxygen containing traces from nitrogen and methane pressure cylinders together with some oxygen adsorbed on the reactor wall are sufficient for its remarkable production.

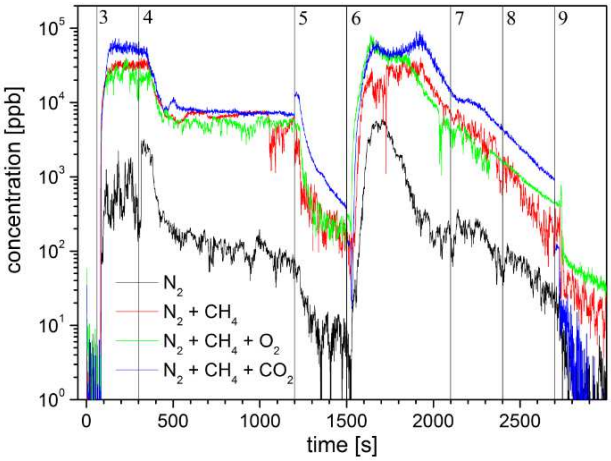

Fig. 5. Concentration of hydrogen cyanide during the second experiment. The vertical lines indicate experimental setting points given in Table 1. Note that saturation limit for the used detection technique is about 60 000 ppb for this compound.

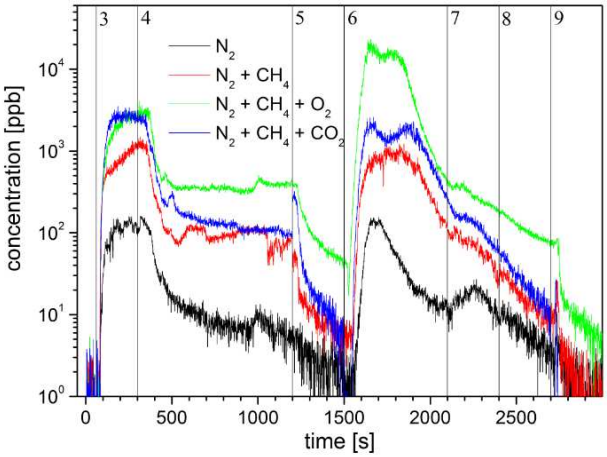

Fig. 6. Concentration of formamide during the second experiment. The vertical lines indicate experimental setting points given in Table 1.

4. Conclusion

The presented contribution brings the first experiments obtained in the Titan like atmosphere at relevant temperature and pressure. The shown pilot experimental data demonstrated the important role of temperature for the formation of different molecules. The experimental data also demonstrated the critical role of the small oxygen containing impurities mainly in the formation of formamide that is known as a nucleic acids bases compounds precursor. Further detailed experiments will be done to verify the role of the discharge operation power and duration as well as the role of other impurities and surface reactions, especially at low temperature. It will be also necessary to develop a complex kinetic model in order to understand the complex chemistry initiated by electrical discharges in this prebiotic atmosphere.

5. References

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