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Atmospheric pressure glow discharge generated in nitrogen-methane gas mixture: PTR-MS analyzes of the exhaust gas[⋆]

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Abstract. This paper reports the results of an extensive study of with the in situ mass spectrometry analysis of gaseous phase species produced by an atmospheric plasma glow discharge in N_2-CH_4 gas mixtures (with methane concentrations ranging from 1% to 4%). The products are studied using proton-transfer-reaction mass spectrometry (PTR-MS). HCN and CH_3CN are identified as the main gaseous products. Hydrazine, methanimine, methyldiazene, ethylamine, cyclohexadiene, pyrazineacetylene, ethylene, propyne and propene are identified as minor compounds. All the detected compounds and their relative abundances are determined with respect to the experimental conditions (gas composition and applied power). The same molecules were observed by the Cassini-Huygens probe in Titan's atmosphere (which has same N_2-CH_4 gas mixtures). Such, experiments show that the formation of such complex organics in atmospheres containing C, N and H, like that of Titan, could be a source of prebiotic molecules.

1 Introduction

Atmospheric pressure glow discharges are of significant interest for a wide range of applications such as pollution control, material processing or surface treatment. Among the many different types of atmospheric pressure discharges the DC glow discharges is one of the most deeply studied [1,2]. The gliding arc configuration has been shown to be a good mimic of planetary atmospheres [3] being used to replicate physical and chemical conditions in Titan. Titan is the largest moon in Saturn's lunar system and the only one with a dense atmosphere (atmospheric pressure is approximately 1.5×10^5 Pa) and thus it has been a subject of interest to astronomers and planetary scientists for more than a century particularly since its atmospheric conditions are thought to resemble those conditions on the Earth several billion years ago [4–6]. It is the only lunar body with a substantial containing significant quantities of carbon (CH_4) and nitrogen (N_2) in its atmosphere [7–9]. Chemical processes in Titan's atmosphere are therefore able to create complex molecules containing C, N and H. This makes Titan our only planetary-scale laboratory for the synthesis of complex organics molecules [10]. In Titan's atmosphere, the dissociation of N_2 and CH_4 by solar ultraviolet radiation initiates chemical reactions that result in the formation of complex organic molecules. The aggregation and heterogeneous chemistry of these molecules produces the aerosols responsible for Titan's orange colour and thick haze layers.

The recent (and on-going) study of Titan by the Cassini-Huygens space mission has revealed its atmosphere contains a rich cocktail are nitriles (HCN, HC_3N, HC_5N, C_2N_2) all believed to be formed as a result of dissociation of nitrogen and methane either by solar induced photolysis or by electron impact [5,11,12] and a large number of hydrocarbons (C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_3H_4) [11,13,14].

In order to induce a nitrogenous chemistry and to study electron-molecule and ion-molecule reactions in planetary atmospheres, experiments have been developed using different plasma discharges (dielectric barrier discharge, gliding arc or corona discharges) to produce the energy delivered to Titan's atmosphere that can induce the aforementioned chemistry [15–22] demonstrating that various complex compounds can be formed, for example the higher hydrocarbons, nitriles or even amino acids.

The present work is focused on the experimental study of gaseous products produced in an atmospheric pressure glow discharge fed by N_2-CH_4 gas mixtures with CH_4 concentrations in the range from 1% to 4%.

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These concentrations are typical of those in Titan's middle and lower atmosphere where pressure may actually exceed those of Earth. The gaseous products were measured qualitatively as well as quantitatively for different methane concentrations in nitrogen by proton-transfer-reaction mass spectrometry.

2 Experimental apparatus

A simplified schematic drawing of the experimental set up is presented in Figure 1. An atmospheric pressure DC glow discharge was created between two stainless steel electrodes separated by a 2 mm gap. The electrodes system had standard configuration of the gliding arc discharge but due to low applied power and low gas velocity the discharge is not moving along the electrodes. The discharge was formed in the stable abnormal glow regime with plasma channel of 1 mm in its diameter. The stainless steel vacuum chamber (volume of 1 L) was evacuated by a rotary oil pump to maintain an oxygen free system. The discharge was operated with an applied power in range 4–15 W in pure nitrogen enriched by 1–4% of CH_4 with total flow rate of 200 sccm. The flow rates through the reactor for both methane and nitrogen were regulated using MKS mass flow controllers. The exhaust gas was analysed in-situ by PTR-MS using H_3O^+ ions. This technique allows very fast analysis of compounds with proton affinity higher than, 165 kcal/mol without any sampling, separation and with little fragmentation of the analysed species. Unfortunately, this method is very difficult to use for the absolute measurements due to difficulty in making a detailed calibration of the feed gases. Thus the presented results are only relative. Moreover, it is nearly impossible to distinguish different isomers so further (complementary) experiments using GC-MS are necessary.

3 Results

The first sets of experiments present stability analysis of gas phase products. Typical result for acetonitrile is shown in Figure 2. There is a distinct time evolution in the formation of acetonitrile recorded over 1000 scans lasting some 2 h. The first part is before the discharge ignition. It represents stabilization before measurement and it takes 70 scans. The second part takes place just after the discharge ignition and takes 200 scans during which there is a rapid increase in acetonitrile relative intensity during 20 scans, then the intensity decreases to 6.5×10^{-8} arb. unit. After this, the relative intensity is nearly constant. There is a small deviation at 600 scans which could be result of product saturation. The same dependencies were obtained for other gas products.

According to stability experiments, the PTR spectra were analysed in range 240–700 scans. Representative PTR-MS spectra for the gas-phase products formed in a plasma discharge driven by a 40 mA current, operating at laboratory temperature, in a 200 sccm gas flow, and at atmospheric pressure for 1% of methane (a) and 4% of methane in nitrogen (b) are shown in Figure 3.

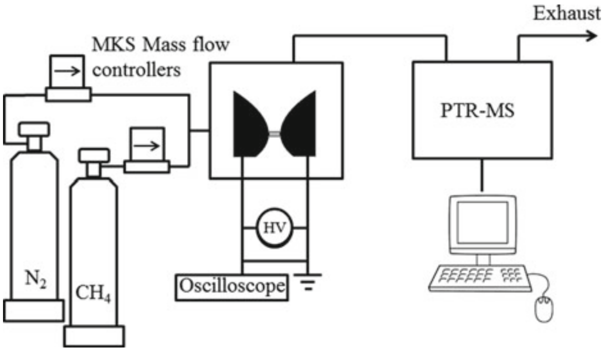

Fig. 1. Schematic diagram of the experimental setup used for PTR-MS analysis of gaseous products of a DC glow discharge fed by various mixtures of N_2-CH_4.

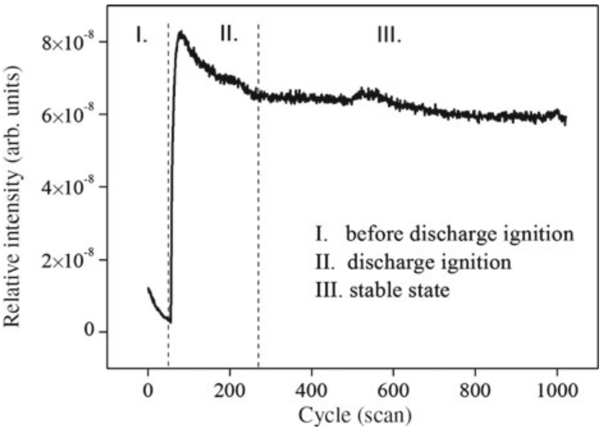

Fig. 2. The time response on the PTR-MS detector system, results for acetonitrile.

The spectra appear to be similar with just a small increase in the peak intensities between 21 and 60 protonated mass. In contrary, a higher intensity of some peaks and some new peaks in the spectra with mass higher than 60 protonated mass can be observed in spectra with 4% of methane.

A higher methane concentration in nitrogen leads to the production of higher molecular weight compounds. So new peaks with higher protonated mass were observed in spectra with 4% CH_4, see Figure 3b. Different ways of synthesis could take place and various complex species can be created under these conditions. Moreover, the solid hydrocarbons were formed on the walls inside the reactor as well as at electrodes during the experiments with higher concentration of methane. The quantity of solid hydrocarbons was seen to increase with increasing methane concentration. These deposits have not been analysed under the presented study.

The main product compounds with their protonated masses are listed in Table 1. The product compounds can be divided into two groups (i) nitrile compounds and (ii) hydrocarbons. The peaks at masses 21 and 37 are not listed there because they correspond to D_2HO^+, and H_3O^+-H_2O ions originating in the ionization source [23]. Small amounts of hydrocarbons in the form of acetylene,

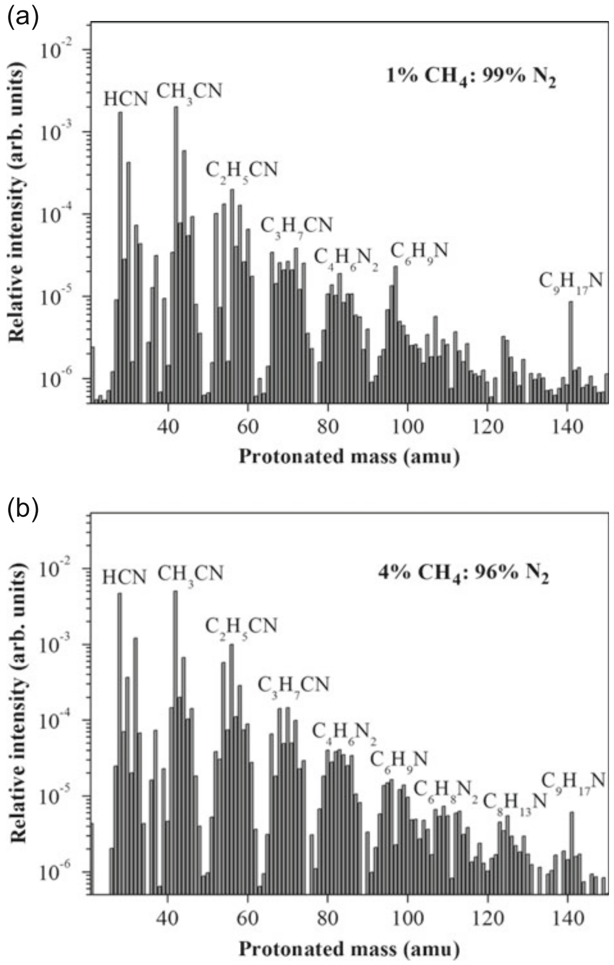

Fig. 3. PTR-MS spectra of the gas-phase products from the reaction of 1% of CH_4 in N_2 (a) and 4% of CH_4 in N_2 (b) gas mixture, flow rate 200 sccm and current 40 mA.

ethylene, propyne, propene, 2-butene and cyclohexadiene were detected. Observation of these species is in agreement with our previous experiments as well as other publications [3,24].

The major products are nitrile compounds. Hydrogen cyanide HCN (proton. mass = 28) and acetonitrile CH_3CN (proton. mass = 42) are the two major products but other nitrile compounds detected are methanimine, methylamine, hydrazine, ethenamine, methyldiazene, ethylamine, propiolonitrile, propenenitrile, proparylamine, 2-propanamine, butanenitrile, 4-methyl-pyrazole, 2,5-dimethl-pyrazole and nonanenitrile. Ammonia (protonated mass is 18) was not observed because the molecular mass is lower than 21 that is the lowest limit for used PTR-MS analytical device.

A quantitative analysis of hydrogen cyanide and acetonitrile under different experimental conditions are given in Figures 4 and 5. These concentrations depend on the discharge current for different methane concentrations in the gas mixtures. Nevertheless the profiles are similar for concentrations between 1% and 4% of methane indeed abundances of hydrogen cyanide and acetonitrile are nearly independent at the higher methane concentrations. The relative intensities of these two selected nitro-compounds decrease with increasing methane concentration in nitrogen gas mixture. The trends of dependencies are similar for all cases, but there is small increasing of intensity (between 25 and 30 mA). It is probably due to experimental uncertainty, because only one measurement was performed.

The formation of various other nitriles (not only HCN and CH_3CN) is assigned to a complex plasma-physical chemistry. Hydrogen cyanide formation can be described by the direct reaction:

$$CH_3 + N \longrightarrow HCN + H_2, \qquad (1)$$

Table 1. The main determined compounds by PTR-MS.

Detected compounds	Formula	Proton. mass	Detected compounds	Formula	Proton. mass
Acetylene	C_2H_2	27	Propiolonitrile	C_2HCN	52
Hydrogen cyanide	HCN	28	Propenenitrile	C_2H_3CN	54
Ethylene	C_2H_4	29	Proparylamine	$C_3H_3NH_2$	56
Methanimine	CH_3N	30	Propanenitrile	C_2H_5CN	56
Amino-methyl	CH_2NH_2	31	Vinylimine	$C_3H_3NH_2$	56
Diimine	H_2N_2	31	2-Butene	C_4H_8	57
Methylamine	CH_5N	32	2-Methylpropene	C_4H_8	57
Hydrazine	H_4N_2	33	Cyclopropylamine	$C_3H_5NH_2$	58
Propyne	C_3H_4	41	2-Propanimine	C_3H_6NH	58
1,2-Propadiene	C_3H_4	41	Dimethyl-diazene	$CH_3N_2CH_3$	59
Acetonitrile	CH_3CN	42	Propanamine	$C_3H_7NH_2$	60
Isocyano-methane	C_2H_3N	42	Butanenitrile	C_3H_7CN	70
Cyclopropane	C_3H_6	43	Cyclohexadiene	C_6H_8	81
Propene	C_3H_6	43	Pyrazine	$C_4H_4N_2$	81
Cyanamide	H_2NCN	43	4-Methl-pyrazole	$C_4H_6N_2$	83
Ethenamine	$C_2H_3NH_2$	44	Pyridinamine	$C_5H_6N_2$	95
Methyldiazene	CH_3N_2H	45	Pyrazole-2,5-dimethyl	C_6H_9N	96
Ethylamine	$C_2H_5NH_2$	46	Benzendiamine	$C_6H_8N_2$	124
Methylhydrazine	$CH_3N_2H_3$	47	Nonanenitrile	$C_9H_{17}N$	140

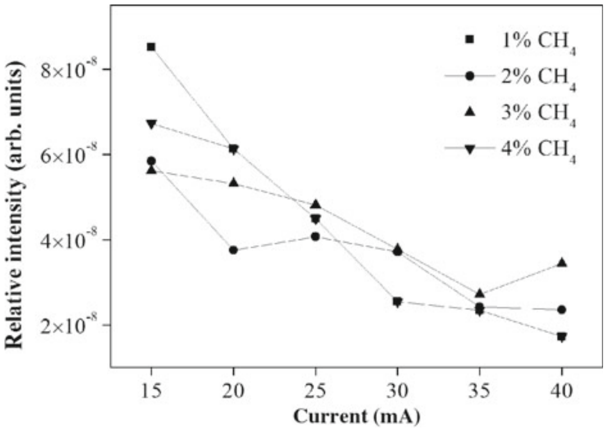

Fig. 4. The dependence of hydrogen cyanide concentrations on discharge current and composition of the gas mixture 1%–4% of methane in nitrogen.

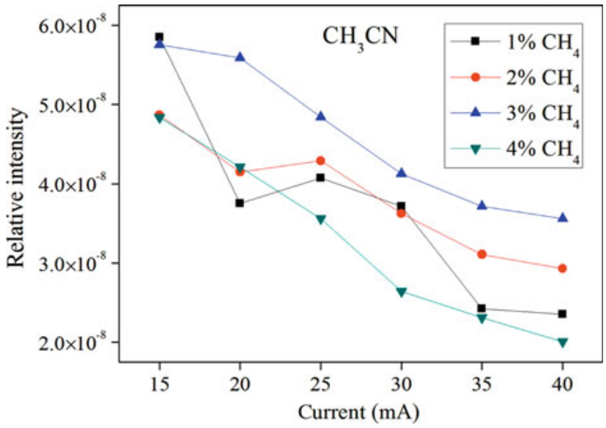

Fig. 5. The dependence of acetonitrile concentrations on discharge current and composition of the gas mixture 1%–4% of methane in nitrogen.

or/and indirect by a two-step process

$$CH_3 + N \longrightarrow H_2CN + H, \tag{2}$$

$$H_2CN + N \longrightarrow HCN + NH, \tag{3}$$

through a highly unstable intermediate product H_2CN [17]. As it is shown in Table 1, nitriles such as hydrogen cyanide, methanimine, methylamine, hydrazine, acetonitrile, ethenamine, methyldiazene, ethylamine, propiolonitrile, propenenitrile, proparylamine, 2-propanamine, butanenitrile, 4-methyl-pyrazole, 2,5-dimethl-pyrazole and nonanenitrile are produced by electron collision reaction and consequent recombination reaction of cyano-groups. The yield and generation rate of nitriles are of the following relationship:

$$\begin{aligned} HCN &> CH_3CN > C_2H_5CN > C_3H_7CN \\ &> C_4H_6N > C_6H_9N > C_9H_{17}N. \end{aligned}$$

The dissociation energies of N_2, CH and CN bonds play an important role in the mechanisms of other nitrile compounds production. Knowledge of the nitriles chemistry has still to be improved. The main detected nitrile compounds were molecular structures with nitrile groups (–CN), amino groups (–NH_2, –NH–, and –N<), and/or imino groups (–C=N–) in our experiments. HCN, CH_3CN and C_2H_5CN have been previously detected in Titan's upper stratosphere, too [5,12,25]. This suggests that the molecules identified in the upper atmosphere can be precursors of the aerosols and that knowledge of their abundance is crucial to the understanding of aerosol chemical formation pathways [5,26]. The overall chemistry is very complicated and unfortunately there is little available data for the bimolecular reactions [27–29]. In the case of atmospheric pressure discharges, these reactions play minor role, only, and more intermediate complexes are formed and thus three body reactions (or indirect reactions with formation of intermediate complexes) are more probable. Data for these reactions are unfortunately very rare.

4 Conclusion

The gaseous phase products formed in the atmospheric glow discharge fed by different mixtures of methane in nitrogen (from 1% to 4%) were determined by in situ PTR-MS analysis. The discharge was operated in the flowing regime at different discharge currents (from 15 up to 40 mA) at laboratory temperature. In situ PTR-MS technique for the exhaust gas phase sampling was successfully used for chemical analysis to deduce the gas composition in the N_2-CH_4 reactive gas mixture mimics of Titan's atmosphere.

Various nitrile compounds and hydrocarbons were observed in all experiments. HCN and CH_3CN were identified as the two major gas phase products with different methane admixtures between 1% and 4%. Small yields of various hydrocarbons were also detected in our experiments. These results are consistent with the Titan's atmospheric composition because the same compounds were detected during the Cassini-Huygens space mission. 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.

The nitriles gas chemistry is still mostly unknown, and nitriles are often ignored in the Titan's atmospheric models even though we know them from direct observations, laboratory mimic experiments and computational models suggest they could be present in large amounts. Atmospheric pressure conditions could play an important role in the chemical processes of hydrocarbons and also nitriles because of high probability of three body reactions or clusters formation. The formation mechanisms of compounds detected on the Titan could be explained by two step reactions between some important intermediates. These molecules including nitrogen are also interesting in exobiology since they are known for their reactivity and as precursors of amino acids.

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