

## The Influence of Admixtures on the Composition of Products by Nitrogen-Methane Atmospheric Glow Discharge

Torokova L.<sup>1,2</sup>, Mazankova V.<sup>1</sup>, Krcma F.<sup>1</sup>, Mason N.J.<sup>2</sup>, Matejcek S.<sup>3</sup>

<sup>1</sup>Faculty of Chemistry, Brno University of Technology, Purkynova 119, 612 00, Brno, Czech Republic

<sup>2</sup>Department of Physics and Astronomy, Open University, Walton Hall, Milton Keynes MK7 6AA, UK

<sup>3</sup>Department of Experimental Physics, Comenius University, Mlynska dolina F-2, 842 48 Bratislava, Slovakia

This work extends our experimentally studies with simulation of Titan's atmosphere by atmospheric glow discharge. This work is devoted to estimate the influence of CO<sub>2</sub> and/or CO on reactivity in the Titan's atmosphere. The exploration of planetary atmosphere is being advanced by the exciting results of the Cassin-Huygens mission to Saturn and Titan, its most famous moon. Most of the studies were mainly interested in the reactivity of the N<sub>2</sub>-CH<sub>4</sub> gaseous mixture and with the primary products of reactions, but the atmosphere of Titan also contains oxygenated volatile species.

**Keywords:** Titan's atmosphere, atmospheric glow discharge, FTIR spectroscopy

### 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  $1.5 \times 10^5$  Pa [4-6]. It is the only lunar body with a substantial containing significant quantities of methane (CH<sub>4</sub>) and nitrogen (N<sub>2</sub>) in its atmosphere [7]. 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 [8]. In Titan's atmosphere, the dissociation of N<sub>2</sub> and CH<sub>4</sub> by solar ultraviolet radiation initiates chemical reactions that result in the formation of complex organic molecules.

The present work is focused on the experimental study of gaseous products produced in an atmospheric pressure glow discharge fed by

N<sub>2</sub>-CH<sub>4</sub> gas mixtures with CH<sub>4</sub> concentrations in the range from 1 % to 4 % plus admixture of carbon dioxide (CO<sub>2</sub>) from 1% to 4 %. The gaseous products were analyzed by Fourier-Transform-Infra-Red spectroscopy (FTIR).

### 2 EXPERIMENTAL APPARATUS

A simplified schematic drawing of the experimental set up is presented in Fig. 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 litre) was evacuated by a rotary oil pump to maintain an oxygen free system. The discharge was operated with an applied power in range 4 to 15 W in pure nitrogen enriched by 1-4 % of CH<sub>4</sub> with admixture of 1-3% of CO<sub>2</sub> 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 analyzed in-situ by FTIR spectroscopy.

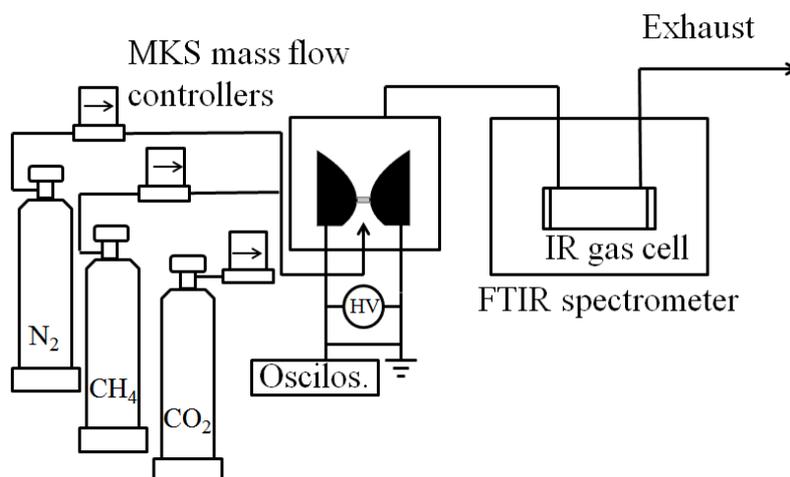


Fig.1: Schematic diagram of the experimental setup used for FTIR analysis of gaseous products of a DC glow discharge fed by various mixtures of  $N_2$ - $CH_4$ - $CO_2$ .

### 3 RESULTS

A typical FTIR spectrum revealing the products formed in the nitrogen discharge fed by 2% of  $CH_4$  and 1% of  $CO_2$  is shown in Fig. 2. Similar spectra were observed for other  $N_2$ - $CH_4$ - $CO_2$  molar ratios. The HITRAN spectral data individual absorption features was used for recognizing of specific compounds. Hydrogen cyanide (HCN) was found to be the most abundant product at wavenumbers of  $1430\text{ cm}^{-1}$  and of  $720\text{ cm}^{-1}$ . The other major

products were ammonia ( $NH_3$ )  $-966\text{ cm}^{-1}$  and acetylene ( $C_2H_2$ )  $-729\text{ cm}^{-1}$  as well as carbon monoxide (CO) and water. These products were recognized in all  $N_2$ - $CH_4$ - $CO_2$  gas mixtures. The products concentrations are strongly depended on compositions of the gas mixture. Increasing the initial  $CH_4$  concentration from 2% to 4% and also increasing admixture from 1% to 3% of  $CO_2$  lead to increase in the products yield.

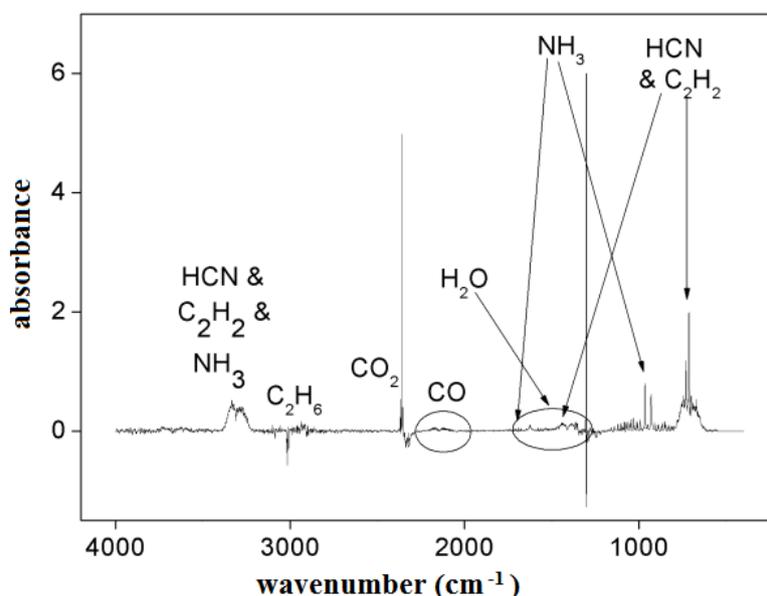


Fig.2: Sample spectrum of analysed products formed in a gas mixture 2% of  $CH_4$  + 1% of  $CO_2$  in  $N_2$ .

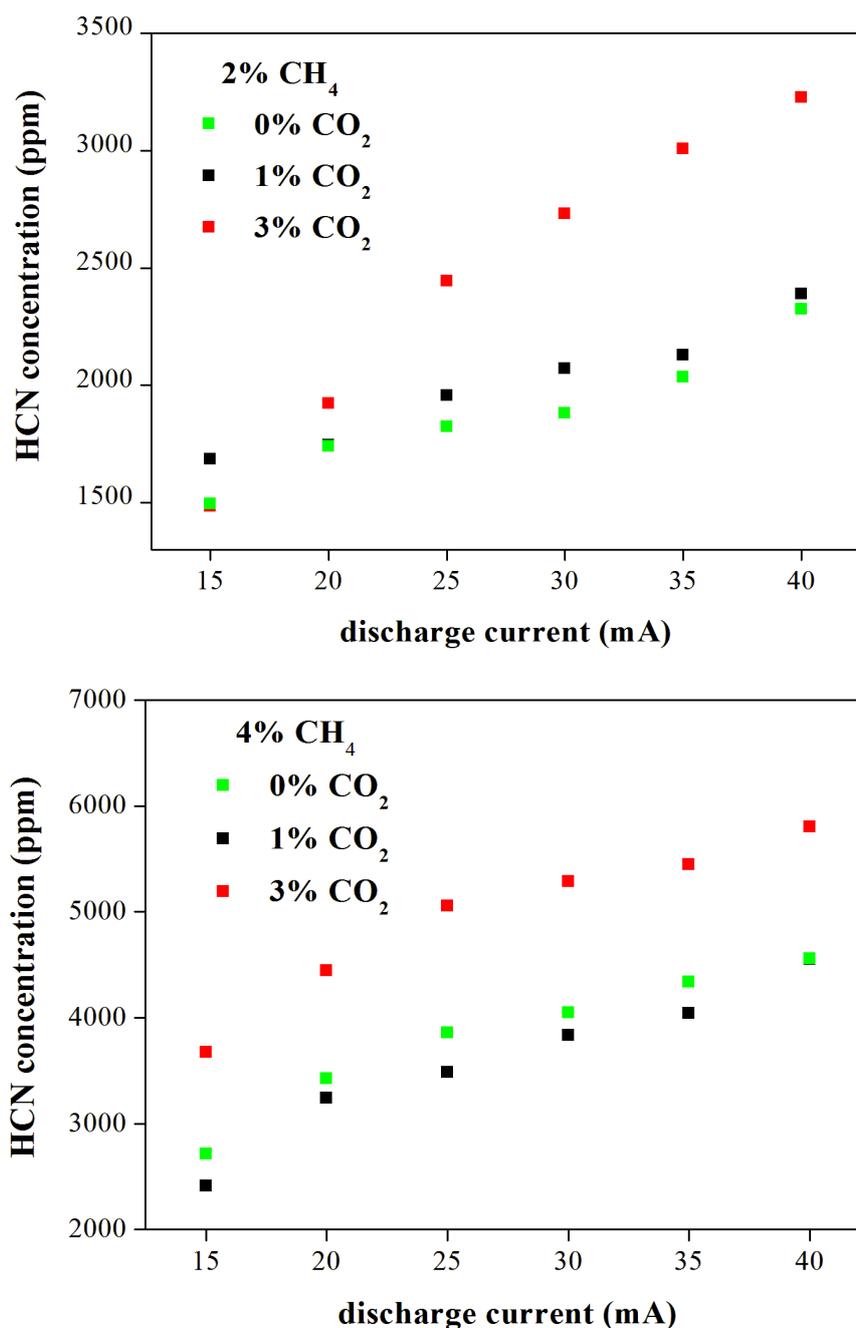


Fig.3: Concentration of hydrogen cyanide dependence on initial concentration of methane and also admixture of carbon dioxide.

Fig. 3 shows the quantitative analysis of HCN at  $1430\text{ cm}^{-1}$  formed under different experimental conditions. Since these experiments have been carried out for different CH<sub>4</sub>-N<sub>2</sub> mixture ratios and the same gas flow rates, the evolution of different product concentrations was found to depend strongly on the initial gas ratios. The dependence of product concentrations is strongly dependent on the different CH<sub>4</sub>-N<sub>2</sub> gas mixtures. On the other hand it was proofed [9] that the kinetics of HCN formation

slows down in presence of CO, showing an inhibiting role of CO on HCN formation. In our experiments this influence was not recognize.

#### 4 CONCLUSION

The gaseous phase products formed in the atmospheric glow discharge fed by different mixtures of N<sub>2</sub> plus CH<sub>4</sub> (2 % and 4 %) and admixture of CO<sub>2</sub> (1 and 3%) were determined by in situ FTIR analysis. The discharge was

operated in the flowing regime at different discharge currents at laboratory temperature. In situ FTIR technique for the exhaust gas phase sampling was successfully used for chemical analysis to deduce the gas composition in the N<sub>2</sub>-CH<sub>4</sub>-CO<sub>2</sub> reactive gas mixture mimics of Titan's atmosphere.

Various nitrile compounds and 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<sub>2</sub>H<sub>2</sub>, NH<sub>3</sub>, CO<sub>2</sub>, CO and also some nitrile oxides. 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.

#### Acknowledgements

This work has been supported by the EUROPLANET TNA2 and CEEPUS network AT-0063.

#### REFERENCES

- [1] Machala Z, Marode E, Laux C O, Kruger Ch, Journal of Advanced Oxidation Technologies 7 (2004) 133.
- [2] Kloc P, Wagner H E, Trunec D, Navratil Z, Fedoseev G, Journal of Physics D-Applied Physics 43 (2010) 34.
- [3] Torokova L, Watson J, Krcma F, Mazankova V, Mason N J, Horvath G, Matejcik S, Contributions to Plasma Physics 55 (2015) DOI 10.1002/ctpp.201400052 – in print.
- [4] Aplin K L, Surveys in Geophysics 27 (2006) 63.
- [5] Lavvas P, Yelle R V, Koskinen T, Bazin A, Vuitton V, Vigren E et al., Proceedings of the National Academy of Sciences of the United States of America 110 (2013) 2729.
- [6] Shebanits O, Wahlund J E, Mandt K, Agren K, Edberg N J T, Waite J H, Planetary and Space Science 84 (2013) 153.
- [7] Horst S M, Tolbert M A, Astrophysical Journal.
- [8] Jagota S, Kawai J, Deamer D, McKay C, Khare B, Beeler D, Planetary and Space Science. 103 (2014) 167.
- [9] Fleury B, Carrasco N, Gautier T, Mahjoub A, He J, Szopa C, et al., Influence of CO on Titan atmospheric reactivity, Icarus, 2014 8//;238(0):221-9.