FTIR analysis of stable gaseous products in N_2-CH_4 atmospheric glow discharge

G. Horvath [1, 2], F. Krcma[3], L. Polachova[2,3], N. J. Mason [2], M. Zahoran [1] and S. Matejcik[1]

[1] *Department of Experimental Physics, Comenius University, Mlynska dolina F-2, 842 48 Bratislava, Slovakia*

[2] *Department of Physics and Astronomy, The Open University, Walton Hall, MK7 6AA, Milton Keynes, United Kingdom*

[3] *Brno University of Technology, Faculty of Chemistry, Purkynova 118. 612 00 Brno, Czech Republic*

1. Introduction

Since Cassini landed on Saturns largest moon, Titan and sent a wealth of data on the atmospheric and surface composition of Titan, many people are focused on the chemistry if its atmosphere. The dense atmosphere of Titan is mostly composed of N_2 with a few percent of CH_4. The most important minor compounds detected by Cassini-Huygens probe are N-containing organics (HCN, HC_3N, HC_5N, C_2N_2) believed to be formed by as a result of dissociation of nitrogen and methane either by solar induced photolysis or by electron impact [1] and hydrocarbons (C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_3H_4 [1, 2]).

Most of experimental works have been performed predominantly in electrical discharges [3-7] which are believed to be a good environment for the study of electron-molecule and ion-molecule reactions.

In this paper we report the results of a new investigation of organic chemistry in atmospheric abnormal glow discharge fed by a N_2-CH_4 gas mixture with CH_4 content in range from 0.5% to 2% using FTIR spectroscopic methods at atmospheric pressure.

2. Experimental set-up

The apparatus used in these experiments is shown schematically in Figure 1. The reactor was connected to the long path IR gas cell equipped with KCl windows and placed in a Nicolet Nexus FTIR spectrometer. The pure CH_4/N_2 gas mixture without plasma was measured as the background spectra. The measurements were carried out in flowing regime for a total flow rate of 200 sccm. The flow rates for both CH_4 and N_2 channels were regulated using MKS mass flow controllers. The discharge electrode system had the standard configuration of a classical gliding arc, a pair of stainless steel holders positioned in parallel to the iron electrodes but in this case the plasma was not gliding due to the low flow rate and therefore stable abnormal glow plasma occurred between the electrodes at their shortest distance of 2 mm, thus forming plasma channel with diameter of 1mm. Electrical parameters have been measured by Tektronix oscilloscope using high voltage probe and 10 Ω resistor for current measurement. The reactor chamber had a volume of 0.3L. The discharge was powered by a home-made DC HV source. The present experiments were performed for different N_2:CH_4 ratios in range from 0.5 % to 2% CH_4 in N_2 at atmospheric pressure.

The discharge power was calculated using the formula

$$P = U \cdot I \qquad \{1a\}$$

where U is the voltage drop across the electrodes and I is the discharge current.

The specific input energy was calculated by the formula

$$\eta = \frac{P}{Q} \quad [\text{kJ/L}] \qquad \{1b\}$$

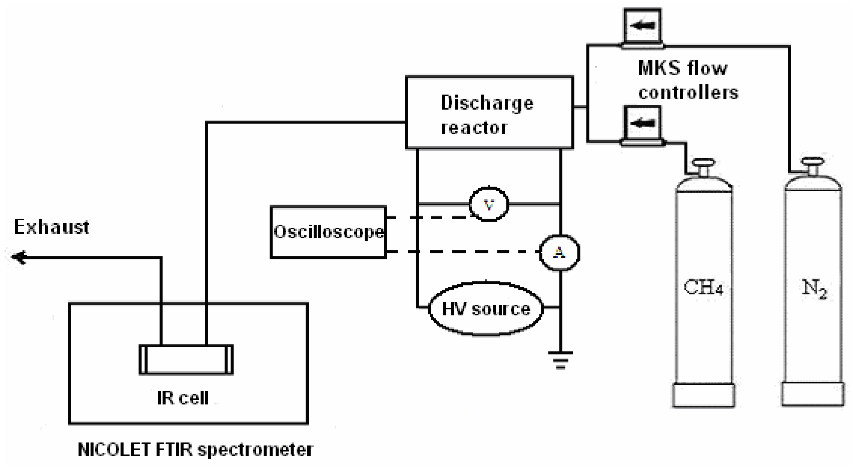


Figure 1. Schematic diagram of the experimental apparatus used for FTIR and OES analysis of gaseous products produced in a gliding arc discharge fed by various mixtures of methane in nitrogen.

where P is the power calculated using {1} and Q is the flow rate. The estimated values were 1.8 kJ/L for the lowest current I = 15 mA and 4.2 kJ/L for the highest current I = 40 mA used in our experiments. The gaseous product concentrations were calculated using the Beer-Lambert formula {2} using IR absorption cross section data found in the HITRAN* database [9]:

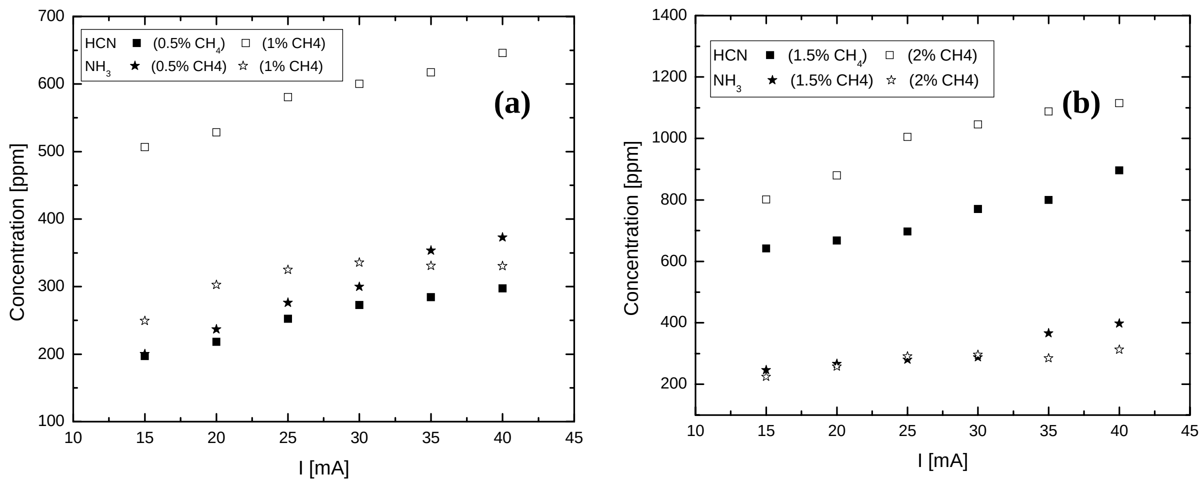
$$A = n.l.\sigma \qquad \{2\}$$

where A is the absorbance measured experimentally, n (cm^{-3}) is the concentration of detected compound, l (cm) is the length of the absorption path in IR cell and σ (cm^2) is the IR absorption cross-section.

All the experiments were carried out at atmospheric pressure and at ambient temperatures. The discharge was typically operated for between 60 and 120 minutes during which time the nascent reactor temperature (as measured by thermocouples on the reactor walls) did not rise above 320 K.

3. Experimental results

The FTIR spectrum obtained for the gaseous products showed different absorption peaks. Besides the remaining CH_4 (3230–2704 cm^{-1}; 1408–1169 cm^{-1}) obvious infrared spectra absorption bands of C≡C were observed at the wave numbers 3386–3217 cm^{-1} which is the typical C-H stretching band of hydrogen cyanide HCN and acetylene C_2H_2. The strongest feature at 713 cm^{-1} is due to HCN, the weak peak at 729 cm^{-1} is due to C_2H_2. However, we found no features corresponding to C_2H_4 (which has a well known band between 800-1100 cm^{-1}, maximum at 956 cm^{-1} and a band between 3000-3200 cm^{-1}, maximum at 3138 cm^{-1}).



Figures 2. The dependence of HCN and NH_3 concentrations on a discharge current for different initial CH_4 concentrations (a: 0.5% and 1%; b: 1.5 and 2%) in N_2 plasma.

In contrast to our earlier measurements made in a coaxial corona discharge [8], NH_3 was observed as a new product in the abnormal glow discharge identified by its strong peak at 966 cm^{-1}, surrounded by dense rotational in range 800-1200. Bands at around 3300 cm^{-1} were overlapped with HCN, NH_3 and C_2H_2. From the measured absorbance values the concentrations of individual compounds were calculated using the Beer-Lambert formula with molecular IR absorption cross-section data being taken from HITRAN spectral database. The dependences of the concentration NH_3 and HCN on the gas flow rate within the frame of discharge power are shown in Figures 2a-2b. C_2H_2, as the minor product did not exceed a concentration 100 ppm during the measurements and it was slightly decreasing with increasing power. It should be noticed that the diatomic molecules such as H_2 were unable to be identified by FTIR. The generation of the energetic electrons has been recognized as the initial step of all the reactions in plasma region. The inelastic collisions of methane molecules with energetic electrons lead to the formation of some active free radicals such as C, CH, CH_2 and CH_3.

It is evident, that the product formation is accompanied by a decrease in concentration of CH_4 but because of possible band overlapping of CH_2 and CH_3 stretching in CH_4 region we were not able to estimate the degree of its decomposition from the measured changes of absorbance in the derivative spectra.

5. Conclusions

In this paper we present the results of a FTIR and OES study of the gaseous products and radicals formed in an abnormal glow discharge fed by 4 different atmospheric pressure mixtures of N_2:CH_4 (0.5, 1, 1.5 and 2 % CH_4) operated in flowing regime at different discharge currents (from 15 up to 40 mA) and ambient temperature. FTIR analysis of the gaseous products showed that HCN, C_2H_2, NH_3 are the main products of our CH_4/N_2 abnormal glow plasma. The yields of these compounds are such that HCN > NH_3 > C_2H_2.

Acknowledgments

This research project was supported by: The Slovak Grant Agency, Slovak Research and Development Agency, Grant UK/381/2009 and UK/389/2008, VEGA 1/0051/08, project SK-CN-0029-07, APVV 0365-07, ESF COST Actions CM0601, CM0805 and EIPAM. Research plan of Czech Ministry of Education No. MSM0021630501.

References

1. V. Vuitton, P. Lavvas, R.V. Yelle, M. Galand, A. Wellbrock, G.R. Lewis, A.J. Coates, and J.-E. Wahlund, *Planet. Space Sci*. in press (2009).
2. S. Vinatier and 10 colleagues, Icarus **188**, 120-138 (2007).
3. Bernard J M, Quirico E, Brissaud O, Montagnac G, Reynard B, McMillan P, Coll P, Nguyen M J, Raulin F and Schmitt B 2006 *Icarus* **185** 301.
4. Sekine Y, Imanaka H, Matsui T, Khare B N, Bakes E L O, McKay C P and Sugita S 2008 *Icarus* **194** 186.
5. Gonzalez R N, Ramirez S I, de la Rosa J G, Coll P and Raulin F 2001, *Adv. Space Res* **27** 271.
6. Ramirez S I, Gonzalez R N, Coll P, and Raulin F 2005 *Advances in Space Research* **36** 274.
7. Plankensteiner K, Reiner H, Rode B M, Mikoviny T, Wisthaler A, Hansel A, Mark T D, Fischer G, Lammer H and Rucker H O 2007 *Icarus* **187** 616.
8. G Horvath, J D Skalny, N J Mason, M Klas, M Zahoran, R Vladoiu and M Manole 2009 *Plasma Sources Sci. Technol.* **18** 034016.
9. http:// www.cfa.harvard.edu/hitran