

# CHEMICAL REACTION STUDIES IN A CH<sub>4</sub>/N<sub>2</sub> GAS MIXTURE OF A DIELECTRIC BARRIER DISCHARGE

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**ABSTRACT.** Chemical reactions in a dielectric barrier discharge at medium pressure of 250-300 mbar have been studied in a CH<sub>4</sub>/N<sub>2</sub> gas mixture by means of mass spectrometry. The main reaction scheme is production of H<sub>2</sub> by fragmentation of CH<sub>4</sub>, but also production of larger hydrocarbons like C<sub>n</sub>H<sub>m</sub>, with n up to 8 including formation of different functional group like amine, nitrile, azole and pyrrole is observed.

## 1. INTRODUCTION

Atmospheric pressure barrier discharge (APBD) are of great interest for application in, e.g., gas chemistry, sterilization, surface activation or thin film deposition [1]. The development of a new process based on this discharge needs a clear understanding of plasma and discharge physics and chemistry. At the present time much attention is paid to the chemical processes in barrier discharge plasma in various gas mixtures, since the understanding of these processes is necessary for the development of industrial reactors [2-3]. We have chosen a gas mixture of CH<sub>4</sub>/N<sub>2</sub> with a gas ratio of 1:2 to investigate physical properties and chemical efficiency of barrier discharges. Nitrogen is abundantly available in the atmosphere and further more a N<sub>2</sub> plasma is more stable to operate than a pure CH<sub>4</sub> plasma. Hence, a mixture of CH<sub>4</sub> and N<sub>2</sub> offers stable plasma conditions. Industrial applications of CH<sub>4</sub>/N<sub>2</sub> gas mixture under consideration are production hydrogen and of higher order hydrocarbon molecules having applications in polymer industries and fundamental plasma chemistry. However, such composition can result in unexpected changes in the physical properties of discharge itself, which can turn into a strong (positive or negative) influence on plasma chemical products [4]. The aim of this work is to study discharge properties of CH<sub>4</sub>/N<sub>2</sub> gas mixture in a high voltage pulsed DBD medium, the influence of the plasma on organic gases and interpretation of the experimental results.

## 2. EXPERIMENT

The experimental set up is shown in figure 1. The plasma chamber is made of stainless steel. The inner dimensions of the chamber are height 12.3 cm, length 18.0 cm, and width 15.0 cm, yielding a chamber volume of 3.32 cm<sup>3</sup>. The two electrodes are made from Ag plates with a length of 8.3 cm, width 3.3 cm, and thickness 0.15 cm.

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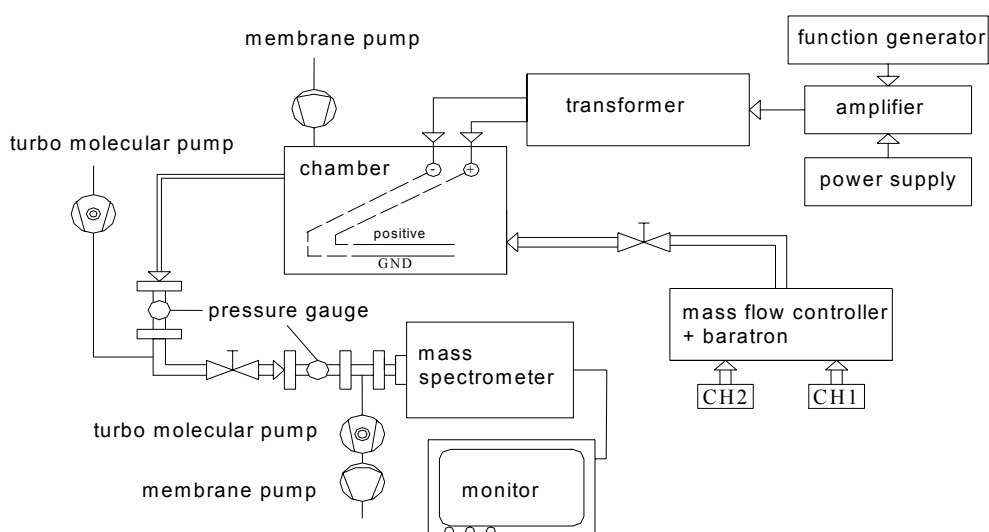


Figure 1: Experimental set-up (schematic)

Both Ag electrodes are covered by dielectrics: the upper (powered) electrode is covered with aluminium oxide ( $\epsilon \sim 10$ ); the lower (grounded) electrode with a glass plate ( $\epsilon \sim 3.8$ ). Both electrodes are separated by 0.15 cm from each other. The upper electrode is connected to a home-built high voltage power supply, while the lower electrode is grounded. The chamber is pumped by a membrane pump down to about 10 mbar. The experiments were performed at a pressure of 250—300 mbar. Pressure inside the plasma chamber was controlled by two gas flow controllers for methane and nitrogen and by an adjustable needle valve between the chamber and the membrane pump. The high voltage power supply consists of a frequency generator delivering a sinusoidal output that is fed into an audio amplifier. The amplifier can be operated at up to 500 W; its output is fed into a spark plug transformer. Experiments were performed at 5.7 kV and at 5.5 kHz. Gas composition of stable reaction products only was detected by a mass spectrometer (Balzers QMS 200). It is pumped by a turbomolecular pump (Pfeiffer TSU 062H) to a base pressure of about  $1 \times 10^{-8}$  mbar increasing to about  $10^{-6}$  mbar during the experiment. A capillary tube of length 103 cm and inner diameter 0.01 cm connects the mass spectrometer with the plasma chamber. A pressure of  $10^{-2}$  mbar at the entrance to the mass spectrometer is maintained during the experiments with the help of a second turbomolecular pump (Balzers 071P).

### 3. RESULTS AND DISCUSSION

Figs. 2 show two mass spectra in the range of mass numbers up to  $m/z=140$  that was obtained after the plasma chamber has been filled with 250 mbar of a  $\text{CH}_4/\text{N}_2$  gas mixture (mixing ratio 1:2). Fig. 2(a) represents the initial gas composition consisting of nitrogen ( $\text{N}_2$ ) and methane ( $\text{CH}_4$ ) gas. Impurities that are present consist, e.g., of oxygen ( $\text{O}_2$ ) and small amounts of higher hydrocarbons around mass numbers  $m/z=40$ , 55, 65, and 78. It should be noted that stable molecules dissociate inside the ion source of the mass spectrometer, giving

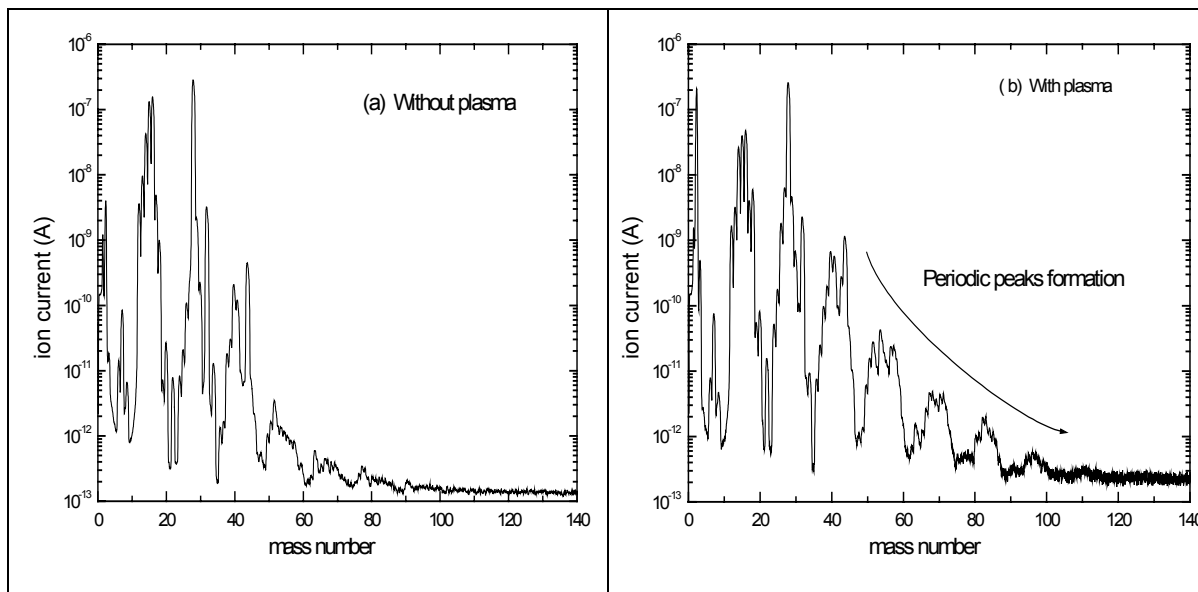


Figure 2 Mass spectra obtained from a  $\text{CH}_4/\text{N}_2$  gas mixture (a) without plasma and (b) after 570 min with the plasma on.

rise to the formation of unstable radical ions that complicate the data analysis [5-6]. For example, methane shows up in the mass spectra with masses  $m/z=16$  ( $\text{CH}_4^+$ ), 15 ( $\text{CH}_3^+$ ), 14 ( $\text{CH}_2^+$ ), 13 ( $\text{CH}^+$ ), and even 12 ( $\text{C}^+$ ). Fig. 2(b) displays the mass spectrum obtained from the same gas after the discharge has been operated for 570 minutes. Several differences compared to fig. 2(a) are noted: (i) a reduction of the methane peaks, (ii) an increase of the hydrogen peak, and (iii) the appearance of higher hydrocarbon peaks. Fig. 3 displays the difference spectrum for mass numbers up to  $m/z = 40$  on a linear scale obtained by subtracting the data of fig. 2(a) from those of figure 2(b).

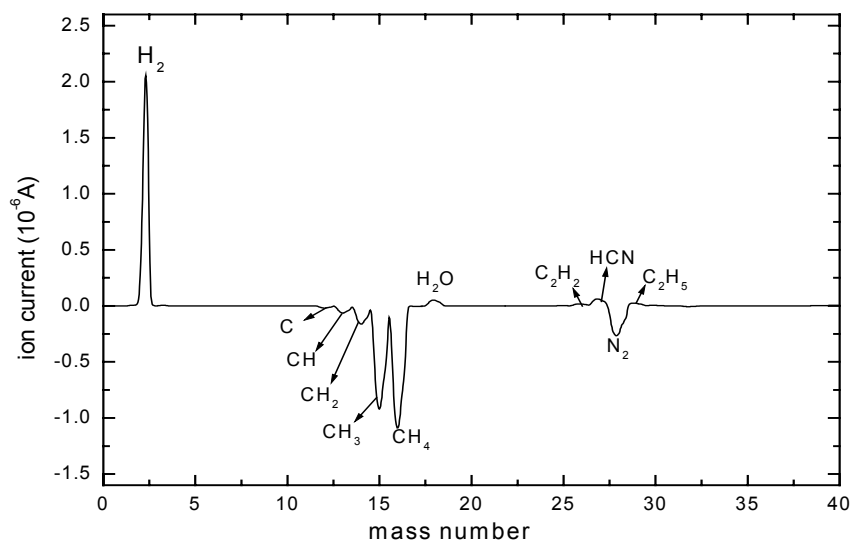


Figure 3 Difference mass spectrum with and without plasma in the mass range  $m/z$  up to 40. Note the linear scale.

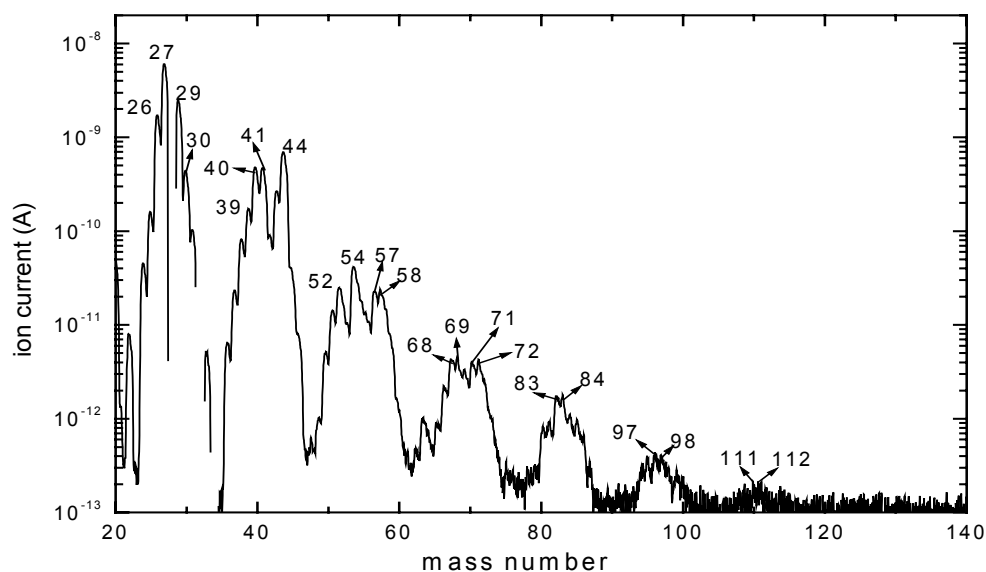


Figure 4: Difference mass spectra with and without plasma in the mass range  $m/z=20-140$ .

From figure 3 the production of a large amount of hydrogen ( $H_2$ ) and a significant consumption of methane, the latter corroborated by the (negative) methane peaks ( $m/z = 12-16$ ), becomes evident. The difference spectrum in the mass range  $m/z=20-140$  is displayed in figure 4 on a logarithmic scale. The broad prominent peaks, each composed of several individual peaks, are attributed to  $C_nH_m$  molecules with  $n$  up to 8 and  $m \approx 2n + 2$ . The most prominent peaks, hence, approximately differ by  $m/z \approx 14$  from each other. Evidently, one  $CH_2$  radical or one N atom is adding up in consecutive reactions and in consequence the spectrum becomes periodic.

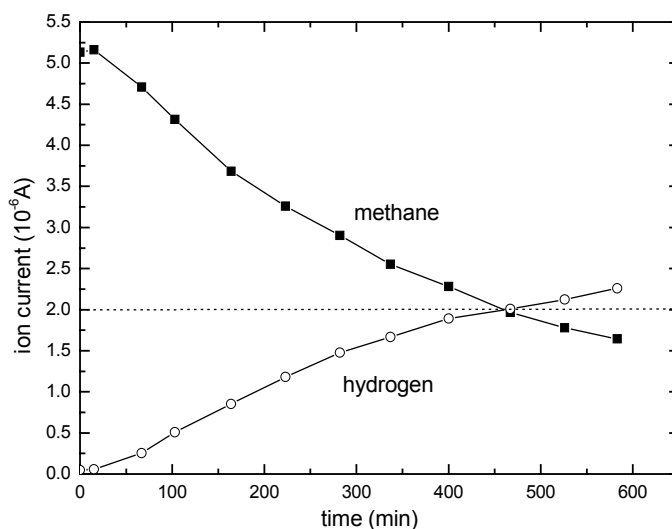


Figure 5: Time dependence of the hydrogen ( $m/z=2$ ) and methane ( $m/z=12-16$ ) peaks.

The time dependency of the hydrogen and methane peaks is shown in figure 5. While the hydrogen peak shows a pronounced increase, the summed methane peaks ( $m/z = 12-16$ ) follow an approximately exponential decay. Taking into account the relative detection efficiency of hydrogen ( $\epsilon \approx 0.8$ ) with respect to methane which was determined in a separate experiment, we note that consumption of a methane molecule contributes to the formation of

an hydrogen molecule roughly on a one-to-one basis. Decomposition of methane leading to the formation of hydrogen molecules is, hence, the dominant chemical reaction in the plasma. Furthermore, it appears that within experimental error bars every consumed methane molecule contributes to the formation of an hydrogen molecule, i.e., a gross reaction scheme,



which may include several reaction steps and eventually is followed by other reactions obeying the gross reaction scheme



seem to apply. However, the relatively small amount of observed  $C_{n+1}H_{m+2}$  molecules compared to  $C_nH_m$ , if not obstructed by low vapour pressure and small detection efficiency, requires other  $CH_2$  consuming processes, too.

In fact, a significant amount of the consumed methane is deposited as a thin film on the electrodes [7]. Preliminary investigations employing x-ray photoelectron and infrared spectroscopy techniques indicate that the deposited film is composed of carbon and nitrogen roughly in a ratio of 2:1 and also contains a significant amount of hydrogen.

In table 1 several prominent peaks and their speculative assignment is shown [8-9]. Apart from the hydrogen ( $m/z=2$ ) and methane ( $m/z =12-16$ ) peaks, the most prominent changes occur at  $m/z=26-30$ .

Mass Number (m/z)	Possible Assignment	Functional group	Relative Intensity
26	CN	Cyanogen	1.7E-9
27	HCN	Cyanogen	6.1E-9
29	C <sub>2</sub> H <sub>5</sub>	Alkane	2.4E-9
30	C <sub>2</sub> H <sub>6</sub>	Alkane	4.2E-10
39	C <sub>3</sub> H <sub>3</sub>	Alkyne	1.6E-10
40	C <sub>3</sub> H <sub>4</sub>	Alkyne	4.5E-10
41	C <sub>2</sub> H <sub>3</sub> N	Nitrile	4.6E-10
44	C <sub>3</sub> H <sub>8</sub>	Alkene	7.1E-10
52	C <sub>2</sub> N <sub>2</sub>	Nitrile	2.4E-10
54	C <sub>4</sub> H <sub>6</sub>	Alkyne	4.1E-11
57	C <sub>3</sub> H <sub>7</sub> N	Amine	2.2E-11
58	C <sub>4</sub> H <sub>10</sub>	Alkane	2.3E-11
68	C <sub>5</sub> H <sub>8</sub>	Alkyne	4.3E-12
69	C <sub>4</sub> H <sub>7</sub> N	Amide	4.5E-12
71	C <sub>4</sub> H <sub>9</sub> N	Amine	4.0E-12
72	C <sub>5</sub> H <sub>12</sub>	Alkane	4.1E-12
83	C <sub>5</sub> H <sub>9</sub> N	Nitrile	1.7E-12
84	C <sub>6</sub> H <sub>12</sub>	Alkene	1.6E-12
97	C <sub>6</sub> H <sub>11</sub> N	Nitrile	4.2E-13
98	C <sub>7</sub> H <sub>14</sub>	Alkene	4.0E-13
111	C <sub>7</sub> H <sub>13</sub> N	Pyrrolidine	2.0E-13
112	C <sub>8</sub> H <sub>16</sub>	Alkene	2.0E-13

Table 1: Observed mass number m/z and their possible assignment.

The peaks at  $m/z = 26$  and  $27$  are attributed to the formation of HCN ( $m/z=27$ ) and its CN ( $m/z = 26$ ) fragment. Likewise, the  $m/z=26$  mass peak may be attributed to the formation of  $C_2H_2$ . Formation of  $C_2H_4$  ( $m/z=28$ ) is likely but its observation is obstructed by nitrogen ( $N_2$ ) consumption. The origin of the mass peak at  $m/z=29$  is usually attributed to a  $C_2H_5$  fragment of larger hydrocarbon molecules, e.g.,  $C_3H_8$  ( $m/z=44$ ),  $C_4H_{10}$  ( $m/z=58$ ) or  $C_5H_{12}$  ( $m/z=72$ ). Many of the prominent peaks can be attributed to molecules containing a CN group, e.g.,  $m/z=26, 27, 52, 57, 57, 69, 71, 83, 97,$  and  $111$ . Hence, most of the observed hydrocarbons species are in the form of alkyne or alkene, nitrile (triple bond carbo-nitrogen), cyclo hexane or pyrroline group[10].

#### 4. SUMMARY

The study focuses on the break down properties of  $CH_4/N_2$  plasma in a dielectric barrier discharge. The dielectric barrier discharge yields to a pronounced break-up of  $CH_4$  and the formation of  $H_2$  molecules. In addition, larger hydrocarbons  $C_nH_m$  with  $n$  up to 8 and nitrogen containing hydrocarbon molecules are observed.

#### 5. ACKNOWLEDGEMENTS

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