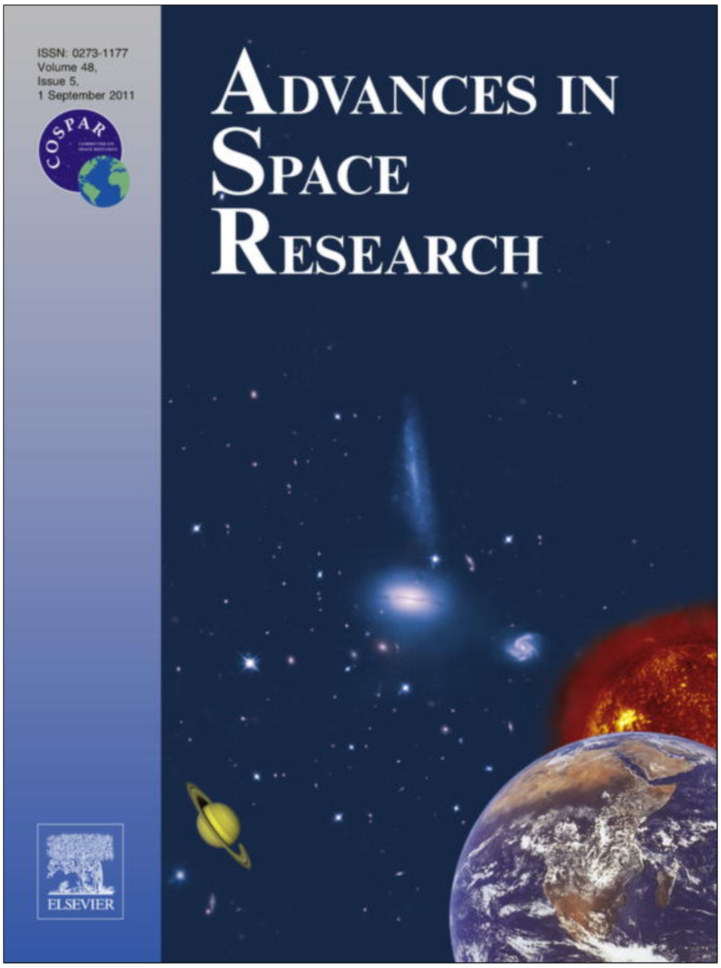
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Plasma chemical reactions in C_2H_2/N_2, C_2H_4/N_2, and C_2H_6/N_2 gas mixtures of a laboratory dielectric barrier discharge

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Abstract

Plasma chemical reactions in C_2H_2/N_2, C_2H_4/N_2, and C_2H_6/N_2 gas mixtures have been studied by means of mass spectrometry at a medium pressure of 300 mbar in a laboratory dielectric barrier discharge. A major reaction scheme is production of larger hydrocarbons like C_nH_m with n up to 12 including formation of functional CN groups.

Keywords: Plasma chemistry; Planetary atmosphere; Tholin

1. Introduction

The atmospheric pressure barrier discharge is of great interest for many applications in, e.g., gas chemistry (Majumdar et al., 2005; Kozlov et al., 2000a,b), sterilization (Fridman et al., 2007; Laroussi, 2008; Majumdar et al., 2009), surface modification (Tajima and Komvopoulos, 2007; Dorai and Kushner, 2003), and thin film deposition (Sonnenfeld et al., 2002). The development of new processes based on this discharge needs a clear understanding of plasma and discharge physics and chemistry. In this communication we present a comparative study of chemical reactions in C_2H_m/N_2 ($m = 2,4,6$) hydrocarbon gas mixtures. Hydrocarbons contribute to greenhouse effect and play an important role in the chemistry of the Earth's and, in particular, Titan's atmosphere (Waite et al., 2005; Teanby et al., 2007; Khare et al., 1984; Kunde et al., 1981; Keller et al., 1998). For example, nitrogen-rich organic substances, so-called tholins, produced by the irradiation of gaseous mixtures of nitrogen and methane are found on Titan (Sagan and Khare, 1979; Cui et al., 2009). The aim of this work is to study plasma chemical reactions of C_2H_m ($m = 2,4,6$) and N_2 gas mixtures in a laboratory pulsed high voltage dielectric barrier (DBD) discharge and interpretation of the experimental results. Laboratory experiments have provided valuable information about plasma chemical reactions leading to the formation of, e.g., organic molecules including amino acids and for the simulating of chemical evolution in planetary atmospheres (e.g., Plankensteiner et al., 2007).

2. Experiment

The experimental set up has been described before (Majumdar et al., 2005; Majumdar and Hippler, 2007). Very briefly, it consists of a plasma chamber with inner dimensions for height, length and width of 12.3 cm, 18.0 cm, and 15.0 cm, respectively. The two electrodes are made from copper plates with a length of 8.3 cm, width 3.3 cm, and thickness 0.15 cm. The upper (powered) electrode is covered with aluminium oxide ($\epsilon \approx 10$) and the lower electrode with a glass plate ($\epsilon = 3.8$). Both electrodes are separated by 0.15 cm from each other. Electrodes were carefully cleaned (or replaced) before each experiment and, in particular, the film deposited during previous experiments was completely removed. The chamber is pumped

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by a membrane pump down to less than 10 mbar. The experiments were performed at a pressure of 300 mbar. The pressure inside the plasma chamber was controlled by two gas flow controllers for the hydrocarbon and nitrogen gases 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. In order to measure the discharge power a small capacitor ($C = 10$ nF) is placed in series between the lower electrode and ground. The voltage applied to the powered electrode and the voltage at the lower electrode are measured with a high voltage probe and serve as x and y inputs of a digital oscilloscope. The discharge power (about 2–5 W) is calculated from the resulting Lissajous figure using the standard method based on the area enclosed by the curve (Wagner et al., 2003; Majumdar and Hippler, 2007) and was kept constant during the experiments.

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 1×10^{-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. The capillary tube is connected to the chamber's wall in a distance of about 5 cm from the electrodes. The tube is necessary to maintain the pressure difference of up to one atmosphere between the plasma chamber and the mass spectrometer. 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).

Gas composition was continuously monitored. Mass spectra were taken every hour at typical sampling rates of 0.5–1 mass numbers per second. The long term stability was investigated for a CH_4/Ar gas mixture with a varying hydrogen admixture (Majumdar et al., 2005) and, in order to check the stability at larger mass numbers, for a C_2H_4/Ar (300 mbar) gas mixture with a varying SF_6 admixture (up to 100 mbar). A linear relationship between SF_6 count rate and SF_6 partial gas pressure was observed. As a further test, mass spectra were recorded over several hours and no signal distortions of relevance were noted.

Fig. 1 displays two typical mass spectra up to mass numbers $M/Z = 180$ that were obtained after the chamber has been filled with 300 mbar of a C_2H_4/N_2 gas mixture (mixing ratio 1:2). Fig. 1(a) represents the initial gas composition consisting of nitrogen and ethylene (C_2H_4) gas. Impurities that are present consist, e.g., of water (H_2O, $M/Z = 18$) oxygen (O_2, $M/Z = 32$) and small amounts of higher hydrocarbons and of other gas impurities around mass numbers $M/Z = 39$–41 (e.g., C_3H_4, Ar), 44 (CO_2), and 50–58 (e.g., C_4H_6, C_4H_8). It should be noted that stable molecules dissociate inside the ion source of the mass spectrometer, giving rise to the formation of unstable radical ions that complicate the data analysis (Boufendi and Bouchoule, 1994; Boufendi et al., 1994). For example, ethane ($M = 30$) shows up in the mass spectra with masses $M/Z = 12$ (C^+), 13–15 (CH_n^+, $n = 1$–3), 24 (C_2^+), and 25–30 ($C_2H_n^+$, $n = 1$–6). Hexane ($M = 86$), on the hand, prominently shows up at mass number $M/Z = 27$, 29, 41–43, 56, 57, and only weakly (with about 4%) at 86. Information about fragmentation patterns have been derived from the NIST Chemistry WebBook (Linstrom and Mallard, 2010).

Fig. 1(b) displays the mass spectrum obtained from the same gas after the discharge has been operated for 360 min. The long operation times had to be chosen because of the small discharge power consumed by the plasma. Several differences compared to Fig. 1(a) are noted: (i) a reduction of the ethylene peaks, (ii) an increase of the hydrogen peak, and (iii) the appearance of higher hydrocarbon peaks with up to 12 carbon atoms. The experimental results presented below are obtained by subtracting the mass spectra obtained without plasma from those obtained with plasma, e.g., by subtracting the data of Fig. 1(a) from those of Fig. 1(b).

3. Results and discussion

In the following we separately present our results for the three C_2H_2/N_2, C_2H_4/N_2, and C_2H_6/N_2 gas mixtures.

3.1. C_2H_2/N_2

The difference mass spectrum from the C_2H_2/N_2 gas mixture in the mass number range $M/Z = 30$–180 is displayed in Fig. 2. A certain amount of the consumed C_2H_2 is used for the production of higher chain hydrocarbons which show up at mass numbers $M/Z = 49$–50 (butadiyne, C_4H_2) and 74 (hexatriyne, C_6H_2). Formation of cyclic hydrocarbons with mass numbers $M/Z = 78$ (benzene, C_6H_6), 92 (toluene C_7H_8), and eventually 106 (e.g., dimethyl-benzene or ethyl-benzene, C_8H_{10}) also occurs. Benzene and other ring components play a role in, e.g., Jupiter's atmosphere and the following reaction pathway for benzene formation has been proposed recently (Wong et al., 2003)

$$C_2H_2 \xrightarrow{CH} C_3H_2 \xrightarrow{H} C_3H_3 \xrightarrow{C_3H_3} C_6H_6. \quad (1)$$

The peak appearing at mass number $M/Z = 52$ (cyanogen, C_2N_2) is readily associated with formation of a nitrogen-containing molecule (Kunde et al., 1981), as was inferred from own measurements without nitrogen where this peak is absent.

While about 50% of the C_2H_2 gas was consumed during the experiment, a crude estimate shows that only about 1% is converted into larger hydrocarbons and less than 0.3% into nitrogen-containing molecules. It is well known that the prominent plasma chemical reactions in acetylene

$$C_nH_2 + CH \rightarrow C_{n+2}H_2 + H \quad (2)$$

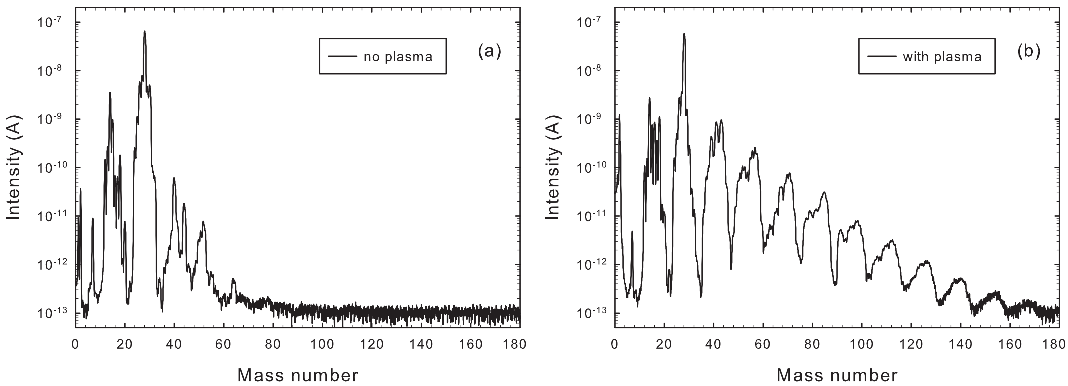

Fig. 1. Mass spectra obtained from a C_2H_4/N_2 gas mixture without plasma (a) and after 360 min with the plasma on (b).

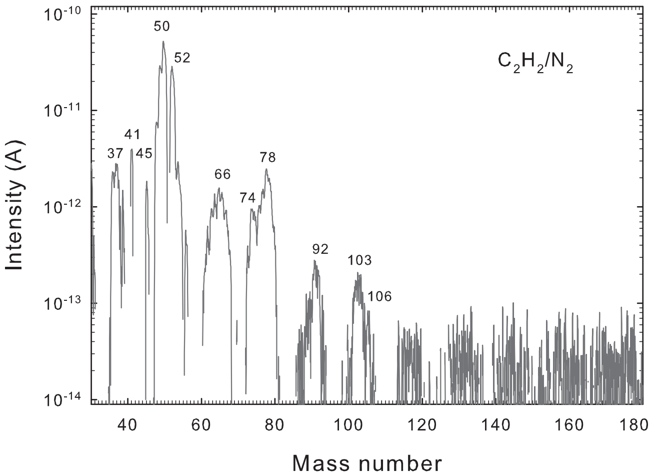

Fig. 2. Difference mass spectrum with and without plasma in the mass number range $M/Z = 35$–180 for a C_2H_2/N_2 gas mixture.

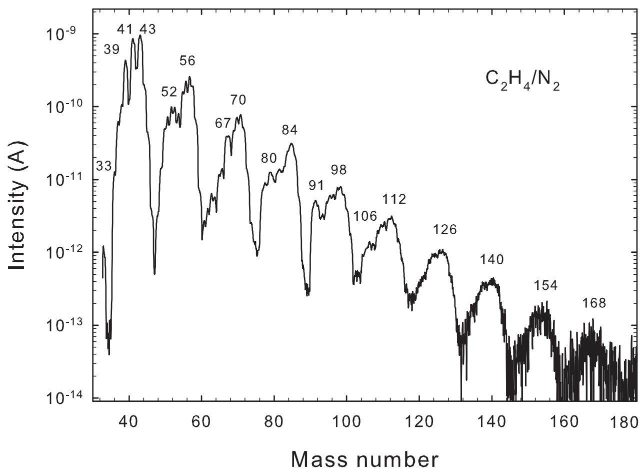

Fig. 3. Difference mass spectrum with and without plasma in the mass range $M/Z = 35$–180 for a C_2H_4/N_2 gas mixture.

lead to the formation of hydrogen-poor molecules which quickly grow to form nanometer- and micrometer-size (so-called dust) particles (Winter et al., 2009; Do et al., 2005, 2009; Mao et al., 2008). Dust formation was not observed in the present experiment, however, presumably due to the low plasma density and the small plasma dimensions which prevent particle growth. Further, a significant fraction of the consumed acetylene condenses on the electrodes forming a soft film with a brownish color.

3.2. C_2H_4/N_2

The difference mass spectrum from the C_2H_4/N_2 gas mixture at mass numbers $M/Z = 30$–180 is displayed in Fig. 3. A significant amount of the consumed C_2H_4 is used for the production of higher hydrocarbons which show up as prominent peaks at mass numbers $M/Z = 40$–180 corresponding to hydrocarbon molecules with up to 12 carbon atoms. The prominent groups appearing at $m \approx 2n$ ($n = 3$–12) are roughly equally spaced by $\Delta M = 14$ corresponding to one CH_2 group. Evidently, one CH_2 radical is adding up in consecutive reactions, thereby obeying the (gross) reaction scheme

$$C_nH_m + CH_2 \rightarrow C_{n+1}H_{m+2} \qquad (3)$$

and in consequence the spectrum becomes periodic. The actual reaction pathways are more complicated, however. For example, chemical reactions of the most prominent C_2H_3 radical with C_2H_4 will contribute to the formation of, e.g., C_3H_3, C_4H_5, C_4H_6, and C_6H_8 including aromatic molecules like benzene and styrene (Norinaga and Deutschmann, 2007). Peaks appearing at mass numbers $M/Z = 39$, 41, and 43 presumably originate from fragmentation of higher order hydrocarbons yielding among others $C_3H_m^+$ ($m = 3, 5, 7$) fragment ions. As before, the peak at mass number $M/Z = 52$ (cyanogen, C_2N_2) is associated with the formation of a nitrogen-containing molecule. We estimate that about 15% of the consumed C_2H_4 is converted into higher hydrocarbons. Further, a significant fraction of the consumed ethylene condenses on the electrodes forming films/deposits with a brown-orange color.

3.3. C_2H_6/N_2

Fig. 4 displays the measured difference spectrum for mass numbers $M/Z = 30$–180. The broad prominent peaks,

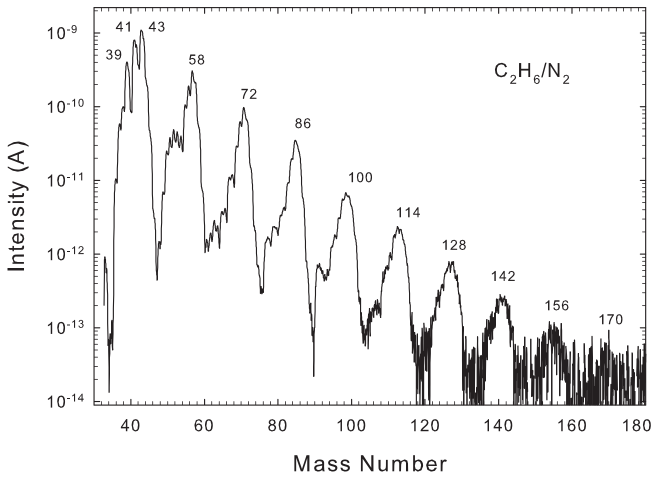

Fig. 4. Difference mass spectrum with and without plasma in the mass range $M/Z = 35$–180 for a C_2H_6/N_2 gas mixture.

each composed of several individual peaks, are attributed to C_nH_m molecules with n up to 12 and $m \approx 2n + 2$. The most prominent peaks, hence, approximately differ by $\Delta M \approx 14$ from each other. Evidently, as in the case of C_2H_4/N_2, one CH_2 radical is adding up in consecutive reactions and in consequence the spectrum becomes periodic. Prominent peaks in the spectrum occurring at $M/Z = 58$, 72, 86, 100, 114, 128, 142, 156, and 170 are attributed to alkane molecules C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$, $C_{11}H_{24}$, and $C_{12}H_{26}$, respectively. Formation of cyclic molecules apparently also occurs, as is inferred from the peaks at $M/Z = 67/68$, 78, 91/92, and 105/106 which are attributed to C_5H_8 (cyclo-pentene), C_6H_6 (benzene), C_7H_8 (toluene or methyl-benzene), and C_8H_{10} (dimethyl-benzene, ethyl-benzene), respectively.

3.4. Comparison of C_2H_2/N_2, C_2H_4/N_2, and C_2H_6/N_2 mass spectra

3.4.1. C_2H_2 and C_2H_4

A comparison of C_2H_2/N_2 and C_2H_4/N_2 mass spectra is made in Fig. 5 (left figure). The following differences are noted:

- the peak positions are shifted to larger mass numbers for C_2H_4 compared to C_2H_2, e.g., $M/Z = 56$ vs. 52, 70 vs. 66, 84 vs. 78, 98 vs. 92, 112 vs. 103 and
- the observed peaks are broader in C_2H_4 compared to C_2H_2

Larger molecules produced from C_2H_4 thus contain a larger number of hydrogen atoms compared to molecules produced from C_2H_2 which are known to be hydrogen-poor.

3.4.2. C_2H_4 and C_2H_6

A comparison of C_2H_4/N_2 and C_2H_6/N_2 mass spectra is made in Fig. 5 (right figure). The following differences are noted:

- A small shift in the peak positions for mass numbers $M/Z > 90$ between C_2H_4 and C_2H_6.
- Peaks in the C_2H_4 spectrum are broader than compared to the C_2H_6 spectrum, except for mass numbers $M/Z = 39$–43.

The latter difference is attributed to the formation of cyclic (aromatic) hydrocarbons which are thus more efficiently produced by C_2H_4 compared to C_2H_6.

3.5. Properties of deposited films

Film deposited on the electrodes during the dielectric barrier discharge in a C_2H_6/N_2 gas mixture display a yellow-brown color. The composition of these films was investigated in some details with the help of X-ray photoelectron spectroscopy (XPS). Accordingly, the film is composed of carbon (C) and nitrogen (N) with N/C ratios of ≈0.2 and ≈0.55 for C_2H_6/N_2 mixing ratios of 1:2 and 1:5, respectively (Martens, 2010). The present results compare favorable with previous investigations of the chemical composition of carbon-nitride films deposited in a CH_4/N_2 dielectric barrier discharge (Majumdar et al., 2007, 2009) where N/C ratios of ≈0.25 and ≈0.6 for a mixing ratios of 1:2 and 1:20, respectively, had been obtained.

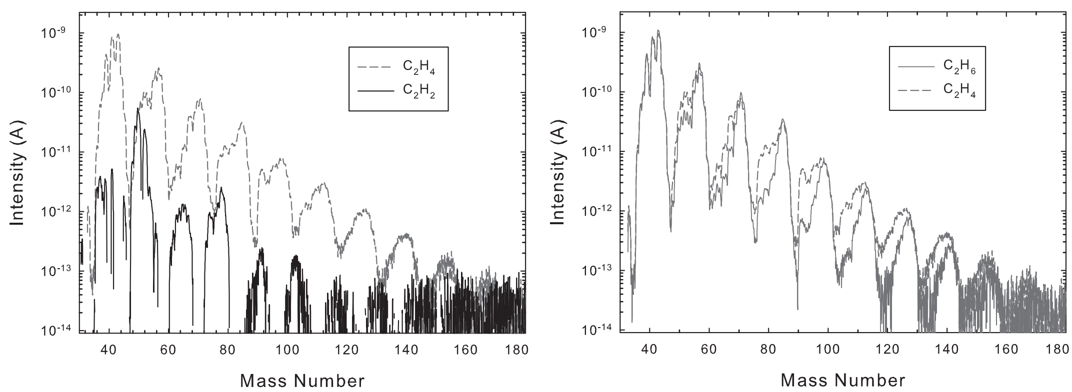

Fig. 5. Comparison of C_2H_2/N_2 and C_2H_4/N_2 (left) and of C_2H_4/N_2 and C_2H_6/N_2 mass spectra with plasma in the mass range M/Z up to 180.

Similar ratios had been observed for films deposited in a C_2H_4/N_2 dielectric barrier discharge plasma (Sarra-Bournet et al., 2010).

4. Summary

A laboratory study of tholin formation in a dielectric barrier discharge with C_2H_2/N_2, C_2H_4/N_2, and C_2H_6/N_2 gas mixtures was performed. Significant differences between the different gas mixtures were noted. In C_2H_2/N_2 the dominant reaction of the formed C_2H radical leads to the formation of the hydrogen-poor molecules C_4H_2 and C_6H_2. In C_4H_2/N_2 and C_6H_2/N_2 gas mixtures formation of large C_nH_m molecules (with n up to 12) including cyclic (aromatic) molecules is observed. About 15% of the consumed C_4H_2 and C_6H_2 is converted into larger hydrocarbons, compared to about 1% of the consumed C_2H_2. In addition, films with a yellow-brown color deposit on the electrodes. Formation of nitrogen-containing molecules appears comparatively weak and only C_2N_2 molecules were identified.

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