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Aromatic compounds in dust forming plasmas

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The formation of aromatic compounds, as for example benzene, is of particular interest not only in the context of gas discharge physics but also for combustion processes and for astrophysical environments. Aromatic compounds have been considered for example to be a candidate for enhanced aerosol formation in the polar region of Jupiter [1] and they are also considered to be important for the generation of soot particles during combustion in hydrocarbon flames. Allamandolla et al. [5] proposed polycyclic aromatic hydrocarbons (PAH) to be the decisive intermediate for the production of carbonaceous interstellar solid particles. According to their model the first step in the formation of PAH's is the production of the phenyl radical C_6H_5 starting from the acetylene molecule. Despite their importance in the fields of astrophysics and combustion theory they are only a few papers [2,3] dealing with the formation of aromatic (hydrocarbon) rings in plasma chemical reactors. We report here about experiments performed in capacitively and inductively coupled (low temperature) hydrocarbon discharges.

Low temperature plasmas can be described as systems being far away from thermodynamic equilibrium. They are characterised by a rather small gas temperature (about room temperature) a moderate ion temperature (about 600 K) and a very high electron temperature (up to 10.000 K- 50.000 K). Although the ionisation degree of such plasmas is usually relatively low (about $10^{-6} – 10^{-4}$) it is this hot electron gas which makes them extremely reactive. The first step in each plasma polymerisation process is the decomposition of the precursor molecule via electron impact dissociation. Reactions as for example

$$C_2H_2 + e^- \rightarrow C_2H + H + e^-$$

lead to an efficient depletion of the acetylene molecule as it is illustrated in figure 1. This figure shows a measurement performed with a mass spectrometer in a capacitiveley coupled discharge operated in a mixture of argon (8 sccm) and acetylene (0.5 sccm). As soon as the discharge is switched on the onset of electron impact reactions leads to the decomposition of acetylene and thus to a decrease of the measured signal. The decrease of the acetylene concentration can be controlled by the rf-input power: the higher the input power the higher the faster the decrease of the acetylene concentration. The sudden change of the slope of the measured signals can be attributed to the formation of dust particles inside the discharge chamber (which was proved by means of laser light scattering). The formation of particles leads to an increase of the electron temperature [4] and thus to an increase of the electron impact dissociation. Consequently we observe a faster depletion of the acetylene component.

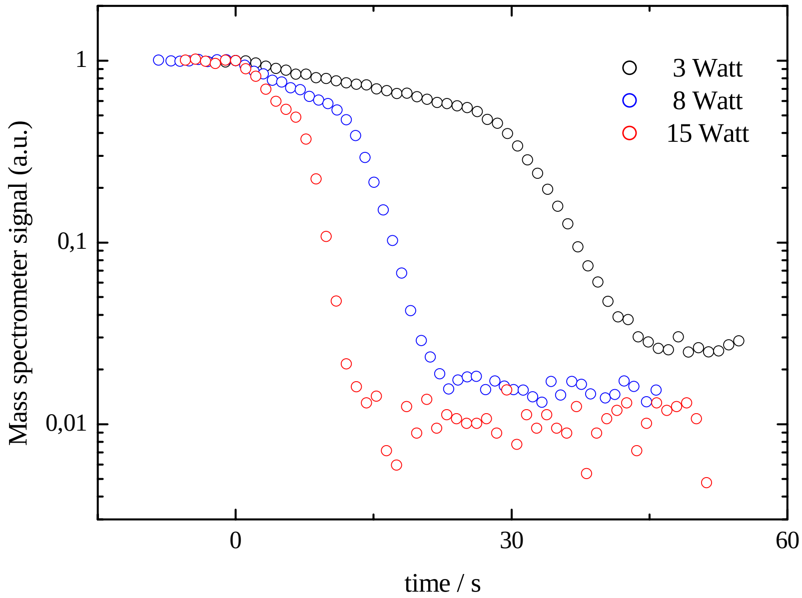
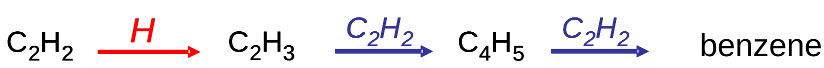


Figure 1: Mass spectrometer signal for mass 26 (acetylene) as a function of time. capacitiveley coupled discharge operated in a mixture of argon (8 sccm) and acetylene (0.5 sccm).

The dissociation of the acetylene molecule leads at the same time to the production of extremely reactive species (radicals) which can themselves initiate very easily subsequent chemical reactions as for example: $C_2H + C_2H_2 \rightarrow C_4H_2 + H$. This reaction of the C_2H radical with acetylene is *one* example that illustrates the way radicals can initiate the formation of larger molecules. *(The reaction is also of particular importance for models of the atmospheres of the outer planets and their satellites, and the product diacetylene (butadiyne). C_4H_2, is a key precursor to the formation of polyacetylene hazes and ices* Pedenen et al. 1993). More complex reaction mechanisms are responsible for the formation of aromatic compounds as for example the benzene molecule C_6H_6. Figure 2 shows the mass spectrometer signal for mass 50 (C_4H_2) and 78 (C_6H_6) as a function of time. A possible reaction pathway (extracted from the reaction scheme presented in [2]) for the formation of benzene is given by:



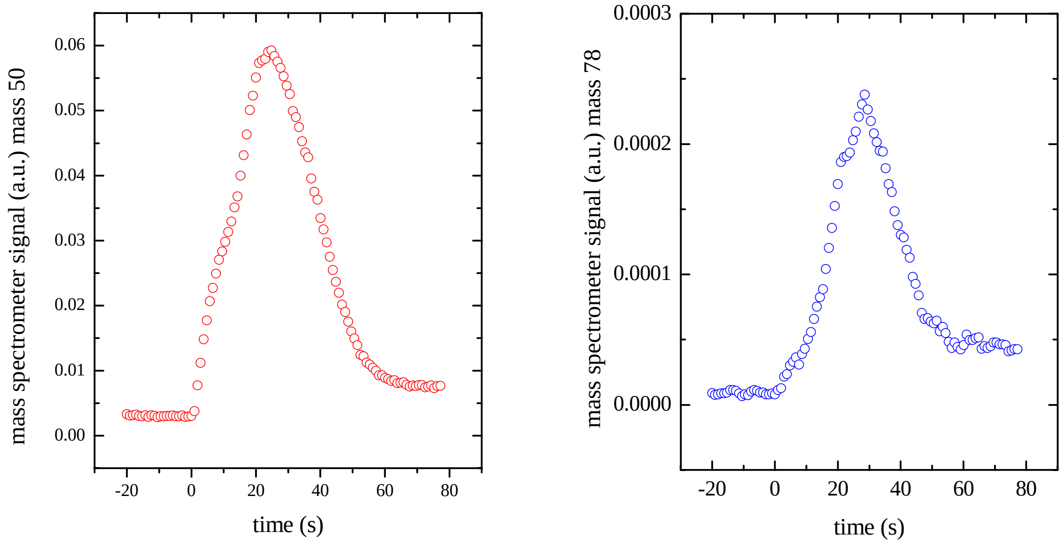


Figure 2: Left view graph: mass spectrometer signal for mass 50 as a function of time. The onset of dust formation occurs at about t = 20 s. Right view graph: mass spectrometer signal for mass 78 as a function of time.

The starting point for the formation of benzene is the C_2H_3 radical which is formed due to the addition of *atomic hydrogen* to the acetylene molecule. The importance of this first step was investigated by means of the dual plasma experiment depicted in figure 3.

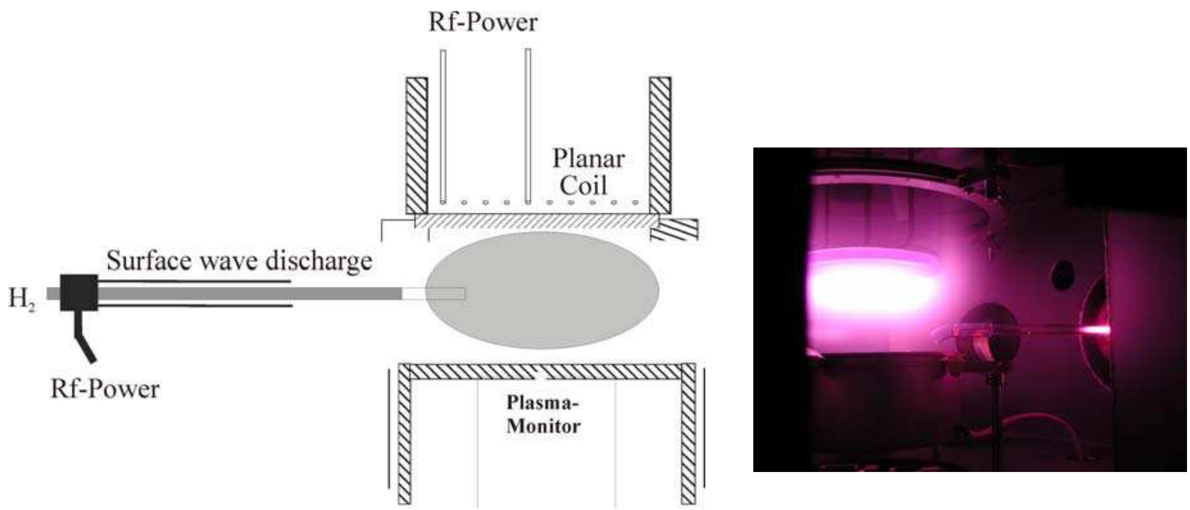


Figure 3: Sketch of the double plasma experiment. The double plasma experiment consists of two parts: the main plasma chamber with the inductively coupled discharge and the surface wave produced plasma running in a glass cylinder that reaches out into the main chamber. The second discharge - that is operated with hydrogen - is used to enhance the amount of atomic hydrogen that flows into the main chamber.

The second discharge in this set up - that is operated with hydrogen - is used to enhance the amount of *atomic* hydrogen that flows into the main chamber The action of this second discharge is illustrated in figure 4. This figure shows the mass spectrometer signal for mass 78 as a function of time. The inductively coupled discharge is running in this experiment in a mixture of acetylene and hydrogen. The acetylene is fed into the main chamber via a ring shaped gas supply. The hydrogen is flowing through the glass cylinder of the second discharge into the main chamber. Important in this experiment is to see what happens when the second discharge is switched on. Exactly this is illustrated in figure 4. In the beginning of the experiment the second discharge is switched off and only molecular hydrogen is introduced into the reaction chamber. Then after approximately 7 minutes the second discharge is switched on. As soon as this happens the intensity of the measured signal clearly increases. When the second discharge is switched off again the signal decreases again and reaches after a short time its original values.

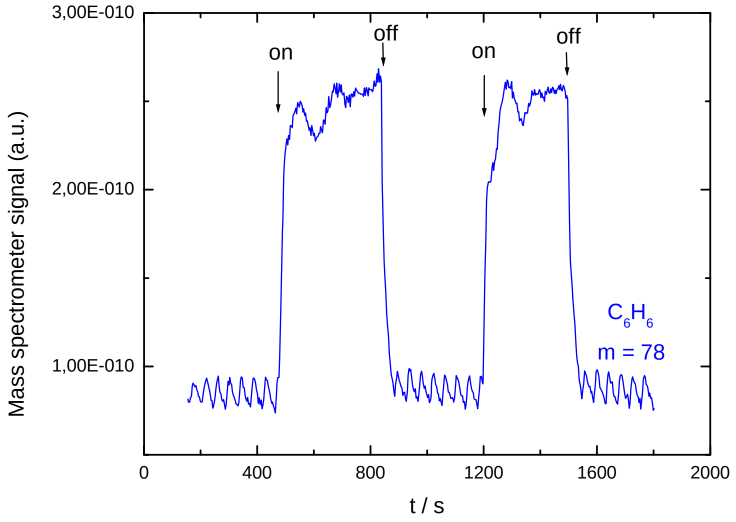


Figure 4: Mass spectrometer signal for mass 78 (benzene) The vertical arrows indicate the time when the second discharge is switched on and off respectively.

This experiment is in agreement with the reaction scheme presented above. The increase of the atomic hydrogen concentration is responsible for the formation of the C_2H_3 radical which is the basis for the production of benzene. The increase of the benzene concentration is only one example for the influence of atomic hydrogen on the chemistry of a hydrocarbon discharge. Further experiments showed that the additional injection of hydrogen atoms leads to a reduction of the polyacetylene formation (C_4H_2,C_6H_2) and even to a suppression of the dust formation.

Literature

1. A.-S. Wong, A. Y. T. Lee, Y. L. Yung, and J. M. Ajello, Astrophys. J. 534, L215 (2000)
2. K.De Bleecker , A. Bogaerts and W.Goedheer, APPL. PHYS. LETTERS 88, 151501 (2006)
3. S. Stoykov, C. Eggs, and U. Kortshagen, J. Phys. D 34, 2160 (2001)
4. I. Denysenko, J. Berndt ,E. Kovacevic, I. Stefanovic, V. Selenin and J. Winter, Phys. Plas. 13,073507 (2006)
5. L.J. Allamandola,, A.G.G.M. Thielens, and J.R. Barker J.R. ApJS,71, 733 (1989)