On the hydrocarbon kinetics in dust producing symmetrically driven rf plasmas

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The chemical phenomena in hydrocarbon containing Ar/He dusty plasmas have been studied combining MIR tuneable diode laser absorption spectroscopy (TDLAS) and Fourier transform infra-red (FTIR) spectroscopy techniques. The experiments were done in a rf cc-coupled parallel plate reactor, f = 13.56 MHz. Using TDLAS the temporal evolution of C_2H_2, C_2H_4, CH_3, CH_4, CO and CO_2 concentrations were measured and the dust particles formation was monitored with FTIR. The values of the calculated fragmentation of the precursor molecules and of the conversion rates of the produced hydrocarbons were in a comparable order of magnitude as they were found in surface wave discharges and in planar microwave plasmas.

The volume chemistry of low temperature molecular plasmas containing hydrocarbon precursors has been of great interest over the past decade [1-2]. This type of plasmas offers a wide field of applications but however a number of processes and properties are far from being fully understood. It is well known, that based on reactions of hydrocarbon precursors, as e.g. acetylene or methane, polymerization processes can lead to the formation of particles with a diameter up to several hundreds of nanometres in the plasma volume [3]. In this case, the analysis of the fragmentation of the precursors and the monitoring of plasma reaction products can lead to a better understanding of basic plasma chemical phenomena.

In this contribution we focused on the hydrocarbon chemistry in relation to dust particle formation in Ar and He RF plasmas of a capacitively coupled parallel plate reactor with admixtures of C_2H_2 and CH_4. Using a compact and transportable multi-component acquisition system (IRMA) combined with an optical long path cell for improved sensitivity the temporal evolution of the concentrations of the methyl radical and of four stable molecules, C_2H_2, CH_4, C_2H_4 and CO has been monitored [4]. To follow the particle growth the temporal evolution of the absorbance was measured by FTIR spectroscopy [3].

All measurements were performed in a radio-frequency (rf) capacitively-coupled parallel plate reactor working at f= 13.56 MHz by an applied power of P= 15 W [5]. During experiments the pressure was p= 0.1 mbar for typical flow rates of 8 sccm Ar, 0.5 sccm C_2H_2 and/or 1 sccm CH_4.

In figure 1 an example of time dependence of concentrations of molecular species measured by TDLAS in Ar and He plasmas with admixtures of C_2H_2 or CH_4 is shown. It can be seen, that after starting the plasma in an Ar-C_2H_2 gas mixture (t = 0 s), concentrations of CH_4 and CH_3 were below the detection limit. After about 10 min, the C_2H_2 flow was stopped and CH_4 was added as precursor. Under these plasma conditions the concentration of the produced species CH_3 and C_2H_2 were found to be in the range of 10^{11} and 10^{12} molecules cm^{-3}, respectively. It is interesting to note, that the concentrations of all hydrocarbon species were strongly correlated with the dynamic of the dust formation.

The degree of dissociation of the precursor gases combined with the *in situ* absorbance measurement at 5000 cm^{-1} of the FTIR system, showing one period of the periodical particle growth from the initiation of the nucleation up to a critical particles size and the disappearance out of the inner reactor volume is illustrated on figure 2. The degree of dissociation of the C_2H_2 precursor was measured by the value of about 95 %. In contrast, the degree of dissociation of the methane precursor varied between 45 and 90 % depending on the appearance of dust particles in the chamber and on the Ar or He plasma conditions. It is well known that the presence of the dust particles can significantly change discharge conditions, especially increase the mean electron energy [6]. With the disappearance of the dust, the mean electron energy decreases and this leads to a reduced degree of dissociation of the precursor gas CH_4, while the density of C_2H_2 is also slightly enhanced.

Using the experimental data concerning acetylene and methane dissociation the absolute fragmentation rates of C_2H_2 and CH_4 and conversion rates to the measured main products CH_4, C_2H_2, C_2H_4 and CH_3 were determined [7]. The fragmentation rates of acetylene were in the range of about R_F (C_2H_2) = 3.2 x 10^{16} molecules J^{-1} and of methane at R_F (CH_4) = 0.16 – 2.5 x 10^{16} molecules J^{-1}. The conversion rates to the produced hydrocarbons were found to be in the range R_C = 0.23 – 8.5 x 10^{14} molecules J^{-1} depending on the discharge conditions in the RF plasma.

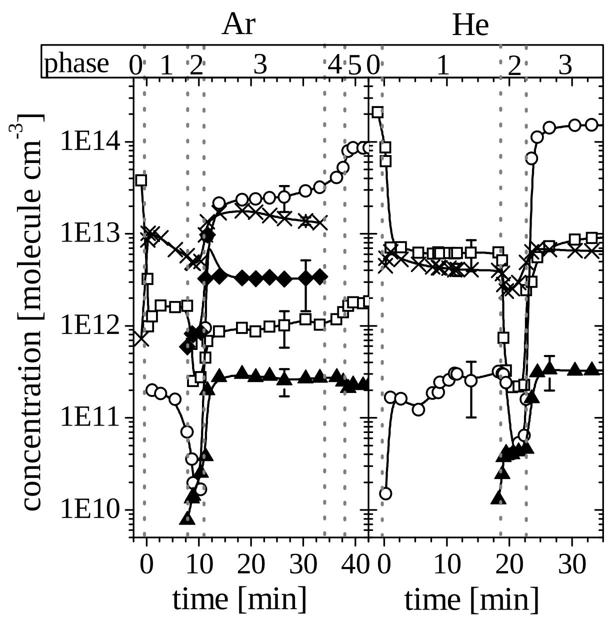

Fig. 1: Molecular concentrations in Ar, left panel, and He RF plasmas, right panel, with admixtures of C_2H_2 or CH_4 in different experimental phases, as a function of the time (□ - C_2H_2, ○ - CH_4, ◆ - C_2H_4, ▲ - CH_3, × - CO).

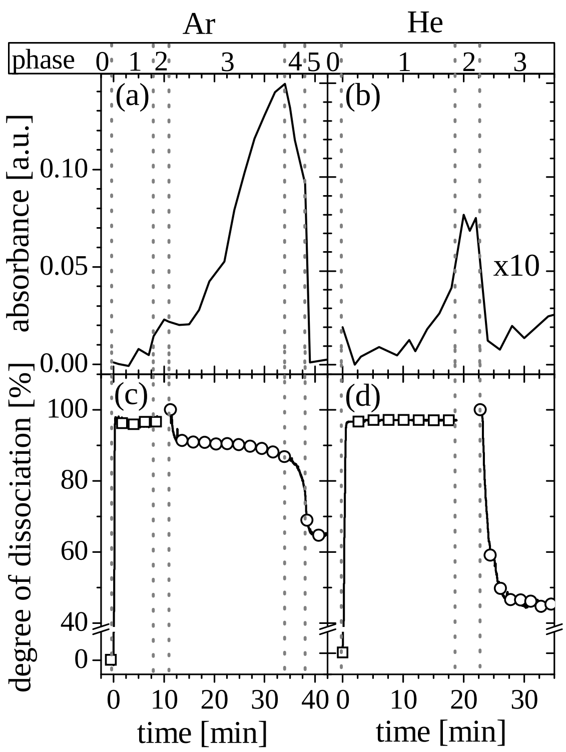

Fig 2: Temporal evolution of (i) the absorbance at 5000 cm^{-1}, measured by FTIR, monitoring the dust production in the reactor (sub-diagrams (a) and (b)) and (ii) of the degree of dissociation of the precursor gases C_2H_2 (□) and CH_4 (○)(sub-diagrams (c) and (d)) in Ar, left panel, and He RF plasmas, right panel, with admixtures of C_2H_2 or CH_4 in different experimental phases.

Acknowledgements

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