Influence of molecular hydrogen on acetylene pyrolysis: Experiment and modeling

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A B S T R A C T

The effect of molecular hydrogen on the formation of molecular carbonaceous species important for soot formation is studied through a combination of shock-tube experiments with high-repetition-rate time-of-flight mass spectrometry and detailed chemistry modeling. The experiment allows to simultaneously measure the concentration–time profiles for various species with a time resolution of 10 µs. Concentration histories of reactants and polyacetylene intermediates ($C_{2x}H_2$, x = 1–4) are measured during the pyrolysis of acetylene with and without H_2 added to the gas mixture for a wide range of conditions. In the 1760–2565 K temperature range, reasonable agreement between the experiment and the model predictions for C_2H_2, C_4H_2, C_6H_2, and C_8H_2 is achieved. H_2 addition leads to the depletion of important building blocks for particle formation, namely of polyacetylenes due to an enhanced consumption of important radicals by H_2, which are required for the fast build-up of carbonaceous material.

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1. Introduction

Clarifying the details of soot formation under a wide range of conditions has been an active research topic for many years with the aim to develop models that can reliably predict soot formation, growth, and burnout. Acetylene is a major decomposition product of several hydrocarbons and plays an important role as a building block towards soot formation. Its thermal decomposition has been studied in a wide temperature range by several authors [1–3]. The most common approach for modeling soot formation relies on the HACA (hydrogen-abstraction, carbon-addition) mechanism [4]. Despite its prominent role, the influence of hydrogen on the formation of soot precursors and soot is not yet fully understood. Hydrogen can either be present as bonding partner in the fuel molecules, or as molecular hydrogen formed during pyrolysis or it can be present as part of the original gas mixture. Already in 1950, Arthur described that the reduction of the H-atom concentration in flames is accompanied with the suppression of flame luminosity, i.e., particle concentration [5]. Recent work aimed at elucidating the influence of hydrogen addition on soot formation and oxidation more systematically [6,7]. However, these theoretical studies so far lack experimental validation, and it is still controversial whether hydrogen promotes or inhibits soot formation [8–11].

In the last two decades many groups shed light on the impact of hydrogen on the soot build-up. Du et al. [12] observed a substantial decrease in the soot inception limit, i.e., a decrease in the soot particle inception rate with hydrogen addition in non-premixed counterflow ethylene, propane, and butane flames. The authors argued that the observed influence of H_2 could be due to chemistry but it could also be explained on purely physical grounds. Gülder et al. [13] demonstrated that for a non-premixed ethylene/air flame, in contrast to propane and butane, the addition of H_2 to the fuel suppresses the soot formation through both dilution and chemistry effects. The reduction of soot by hydrogen in propane and butane flames was suggested to be only due to dilution. In a recent study, Pandey et al. [14] investigated the influence of H_2 addition on soot formation and soot morphology in non-premixed laminar acetylene/air flames with various flow arrangements. They reported that the H_2 addition increases the centerline flame temperature by 50–100 K and that the soot volume fraction decreases with H_2 addition. These findings are in good agreement with results for ethylene, propane, and butane/air flames which have been explained based on the HACA mechanism.

Abian et al. [15] studied the effect of H_2 and typical components of recirculated exhaust gases (CO, H_2O, CO_2) on soot and other gaseous products, that are formed during the thermal decomposition of ethylene. The experiment was carried out in a flow reactor and the results were compared with simulations based on a

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gas-phase kinetics model. They found that the addition of H_2 chemically alters the reaction pathways leading to the formation of soot, and consequently suppresses soot production, due to its direct participation in the HACA mechanism [10]. The effect of H_2 on the oxidation of methane was studied experimentally and modeled with a kinetics model by Cong et al. [16]. They found that H_2 accelerates methane oxidation by producing O, H, and OH. Ruiz et al. [17–19] have studied the soot yield from C_2H_2 and C_2H_4 pyrolysis and its properties in a flow reactor as a function of temperature, initial concentrations, and residence time. More recent investigations dealing with the effect of hydrogen on soot formation can be found in [20–26]. Eremin et al. published a detailed experimental study to elucidate the role of hydrogen on particle growth behind shock waves where temperature, particle sizes and induction times were measured [27]. It was found that the measured temperatures were similar for both cases (with and without H_2 addition) and that H_2 addition increases the induction times and decreases both the particle sizes and optical density of the soot-containing mixture. Böhm et al. [28] investigated the effect of hydrocarbon-bonded (C_2H_2) and molecular hydrogen (H_2) on precursor and particle formation in the pyrolysis of C_3O_2 in argon behind reflected shock waves. It was found that H_2 reduces the particle volume fraction, the mean particle diameter, the particle number density, and the maximum temperature rise of the mixture.

All these works have in common: They investigate the effect of molecular hydrogen in flames or in flow reactors where the main targets were soot particles in the late stage of formation. Shock tubes were also used to elucidate the effect of H_2 on acetylene, but the focus was also set on the consequence of adding H_2 on the optical density of the reaction mixture, on particle sizes, as well as gas temperature. In the present work, the influence of H_2 on carbonaceous reaction intermediates that are important for soot precursor formation in acetylene pyrolysis has been studied in a shock tube that prevents transport phenomena that may interfere with chemical processes in flames and flow reactors. The study contributes to the understanding of soot formation in its early stage by time-resolved measuring absolute concentrations of polyacetylenes considered as potential precursors leading to soot formation. Additionally, a detailed kinetics model was developed to explain the experimental observations.

Shock tubes that are equipped with a variety of modern diagnostics are versatile tools that are widely used for gas-phase reaction kinetics studies [29,30] enabling the investigation of high-temperature reactions on short time scales (up to a few milliseconds). Fast detection methods are required, that provide time-resolved information about the change of composition of the investigated mixture within the test time.

A high-repetition-rate (HRR) time-of-flight mass spectrometer (TOF-MS) can simultaneously measure the concentration–time profiles for numerous species with approximately one measurement every 10 μs. Combinations of shock tubes with TOF-MS are established for the study of complex reaction systems [2,31,32], in particular those that involve soot formation. In the present study, we used a shock tube coupled to a HRR-TOF-MS to investigate the thermal decomposition of acetylene with and without hydrogen behind reflected shock wave in details.

Polyacetylenes are assumed to be "pre-soot" species in pyrolysis and oxidation of most fuels. The direct and simultaneous detection of them gives the possibility to investigate the influence of hydrogen towards soot formation in its earlier stages.

2. Experiment

The experiments are conducted in a stainless-steel diaphragm-type shock tube. Both the driver and driven section have an inner diameter of 80 mm. The driver section has a length of 2.5 m and the driven section measures 6.3 m. Aluminum sheets with a thickness of 50–100 μm are used as diaphragms between the driver and the driven section. Both driver and driven sections are simultaneously pumped down to 4×10^{-2} mbar (Edwards Dry Star, QDP 80). Via a by-pass line, this pump is also used to evacuate the 50 l vessel that is used for preparing the investigated gas mixtures. The driver section is filled via a magnetic valve with the driver gas (here: helium). The pressure in the driver section is measured with a pressure gauge (Keller, Mano 2000) which is also used to measure the diaphragm rupture pressure. The inlet pressure of the reactive mixture (p_1) in the driven section is measured with a pressure sensor (Edwards, Trans 600 AB) usable for pressures up to 1000 mbar. A set of four pressure transducers (PCB-112A05) are positioned at equal distances of 150 mm on the top of the driven section of the shock tube. The fourth transducer is located 150 mm from the end plate. A fifth pressure transducer located close to the end plate measures the reflected-shock pressure. The signals of these pressure transducers are amplified with charge amplifiers (Kistler, Kiag Swiss 5001) and detected by an oscilloscope to determine the shock wave velocity. The pressure and temperature behind the reflected shock wave (p_5 and T_5) are calculated from shock wave equations [33] using the initial pressure and temperature in the driven section (p_1 and T_1) and the velocity of the incident shock wave which is determined from the pressure transducer signals. Attenuation values of the shock velocities give uncertainties in the determined post-shock temperature of around ±15 K.

A precision-manufactured conical nozzle (Frey, 45 μm diameter) is located in the center of the end flange that separates the driven section and the TOF-MS. The distance between the nozzle and the ionization section of the TOF-MS is 8 mm. The TOF-MS (Kaesdorf) can operate at high repetition rates (up to 150 kHz). Both, short flight distance in the TOF-MS and high acceleration voltage ensure short flight times which avoids overlapping of signals from consecutive cycles up to masses of 240 u at 100 kHz. The TOF-MS is equipped with an electron impact ion source with energies in the 5–85 eV range. The maximum kinetic energy of the ions is 10 keV, which is high enough to generate signals for molecular masses up to 1000 u (then, with a maximum repetition rate of 50 kHz). The apparatus is used in reflectron mode and the ions are detected with a micro-channel plate (MCP) detector. More details about the experiment are given in [34].

When the shock wave passes the first pressure transducer (the one farthest from the end flange), a TTL signal triggers the ionization in the TOF-MS and the data of the subsequent mass spectra are acquired by an oscilloscope (Agilent Acquiris). Several full mass spectra are thus detected already before the arrival of the shock wave at the sampling nozzle, which then helps to define the exact zero time of the shock arrival from the sudden rise in signal. Figure 1 shows raw data obtained by the TOF-MS. The sudden increase of the signal intensity is due to the pressure increase behind the reflected shock wave which is accompanied by an increase of the mass flow into the mass spectrometer. Because of the restricted time resolution in this figure, each full mass spectrum is visible as a single peak only with the maximum signal due to the bath gas neon. Neon is chosen as bath gas because of its comparably small ionization cross-section to prevent overloading of the MCP detectors; but because of its high concentration (>90%) it still provides the strongest signal.

The mass-to-charge ratio m/z of the detected ions is determined for each peak from its time of occurrence t.

$$m/z = a(t - b)^2 \tag{1}$$

The constants a and b are determined from calibration measurements with noble gas mixtures. Figure 2 shows a room-temperature