Influence of methane addition on soot formation in pyrolysis of acetylene

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ABSTRACT

Time-resolved laser-induced incandescence for particle sizing and laser light extinction for soot volume fraction was applied simultaneously to study the influence of methane addition on soot formation in acetylene pyrolysis. Three series of the experiments with initial mixtures of 2% C_2H_2 + Ar, 1% CH_4 + Ar and 2% C_2H_2 + 0.5/1/2% CH_4 + Ar in the temperature range of 1600–2300 K and the pressure range of 4–5 bar behind reflected shock waves were carried out. The kinetic characteristic of the soot formation process— the induction time of soot particle inception as well as the temperature dependences of final values of soot volume fraction and particle sizes have been determined and analyzed. An essential increase of soot volume fraction, particle sizes and a decrease of induction time of soot inception at methane addition to acetylene were observed. The gas phase kinetic modeling of the investigated processes up to the soot nuclei precursors formation has been performed. Analysis of gas kinetic stages of acetylene decomposition with methane addition has demonstrated the significant increase of the rates of pyrene formation followed by PAH growth due to effective propargyl C_3H_3 formation.

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1. Introduction

The problem of soot formation during the combustion and pyrolysis of hydrocarbons has been in the focus of attention for many decades. Despite a large amount of experimental and theoretical studies (see for example reviews [1–4] and references within), a number of important issues remain insufficiently studied. One of such problems is the mechanism of soot formation in the pyrolysis of acetylene. A unique feature of acetylene is the presence of a triple bond between carbon atoms at a ratio C/H = 1, which provides an extremely effective formation of polyyne chains during its pyrolysis. However, polyyne molecules are very thermodynamically stable at high temperatures that cause the overprediction of the soot yield if the higher polyynes are directly involved in the formation of soot particle nuclei [5]. In recent years, a number of works have attempted to adapt the HACA mechanism and supplement it with elements from the polyyne model [5–6]. However, there is no universal model that satisfactorily qualitatively and quantitatively describes the formation of soot in acetylene-containing mixtures.

An even greater level of complexity arises describing the formation of soot in binary mixtures. Experimentally, the process of soot formation in binary hydrocarbon mixtures was studied in shock tube pyrolysis [7–8] and flames [9–12] and flow reactor [12]. Observed results indicated that the data on soot formation in various binary mixtures are rather conflicting [7]. Strong decrease of soot was found with addition of hydrogen to shock tube pyrolysis of acetylene [7,8,13] and for the ethylene/air diffusion flame [14], but no affect was found for premixed ethylene flame [9]. Methane addition to ethylene resulted in the increase of PAH in flow reactor and diffusion flame and the increase of soot in diffusion flame whereas experiments in premixed flame did not show any synergetic effect [12]. Oxygen-containing additives caused the oxidation of carbon and mostly the decrease of soot yield in shock tube pyrolysis [15–16] and premixed flames [17]. On the other hand, a small amount of oxygenated additives can promote soot formation due to the peculiarity of blend pyrolysis kinetics [18]. The increase in soot yield was found in non-premixed ethylene flame with partial ethanol replacement as a fuel [19]. For aromatic-acetylenic mixtures both the synergistic and the negative effects of soot yield were observed for pyrolysis and flame conditions [7,8,10].

In this view, it becomes particularly important to obtain new experimental data in the mixtures of acetylene with alkanes, primarily with methane. It is known that the formation of soot in the pyrolysis of methane due to C/H = 0.25 is extremely difficult. On
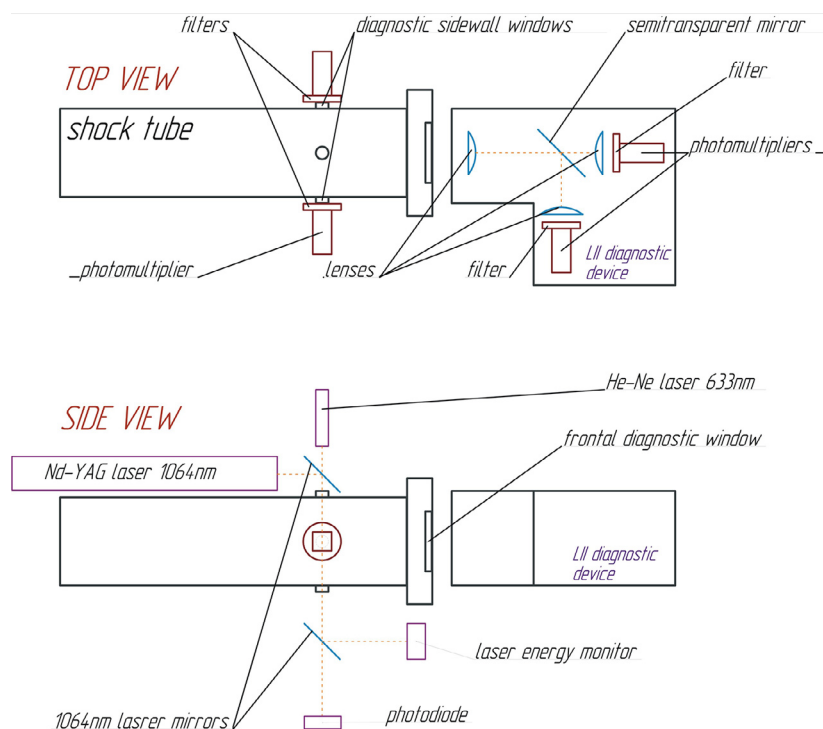
Fig. 1. Experimental setup.

the other hand, when adding methane, additional carbon atoms appear in the mixture, which can lead to an increase in the soot yield, but at the same time a fourfold more hydrogen atoms appear, which, as it is known, should reduce the soot yield. Moreover, the CH_4 molecules in the reacting mixture give different hydrocarbon radicals, which also could have a controversial effect on soot growth. Therefore, the influence of methane additives on the soot yield in acetylene is a priori not obvious.

The preliminary experiments [20] showed that the soot yield in such mixtures substantially increases. Therefore, the purpose of this work was a more detailed experimental and numerical study of this interesting and unexpected effect.

2. Experiment

2.1. Apparatus and mixtures

The experiments were carried out behind reflected shock waves in a conventional stainless steel diaphragm type shock tube with an inner diameter of 50 mm. The driver and the driven section had 1.5 and 3.5 m in length respectively. The values of temperature (T_{RSW}) and pressure (P_{RSW}) behind the reflected shock wave (RSW) were determined based on the measured incident shock wave velocity by applying one-dimensional gas-dynamic theory and assuming frozen reaction conditions. The shock tube was equipped with two PCB113B piezoelectric pressure gauges to measure the incident shock wave velocity with the accuracy of 0.5% that resulted in the T_{RSW} uncertainty about 25 K. The T_{RSW} was varied in the range of 1650–2250 K and P_{RSW} was in the range of 4–5 bar. The shock tube was evacuated by a fore-vacuum pump to a pressure of 4×10^{-2} mbar. After every experiment the inner walls of tube were cleaned several times with an ethanol. The test gas mixtures were prepared manometrically in a stainless steel mixing vessel. The composition of investigated mixtures was 2% C_2H_2 + 98% Ar, 1% CH_4 + 99% Ar, 2% C_2H_2 + 0.5% CH_4 + 97.5% Ar, 2% C_2H_2 + 1% CH_4 + 97% Ar and 2% C_2H_2 + 2% CH_4 + 96% Ar. The purity for C_2H_2 was certified to be 99.9%, for CH_4—99.99%, for Ar—99.999%. Strong

dilution with inert gas in the shock tube reactor is due to two reasons: first, better gas dynamics in a shock tube, which allows obtaining more accurate kinetic data, and, second, the limitations imposed by optical diagnostic methods: the LII and laser extinction. Our experience [13] has shown that in order to avoid saturation of laser extinction, mixtures with no more than 3% acetylene at pressures up to 10 bar should be used. The optical access in the measurement section was given by four calcium fluoride windows of 6 mm in a diameter mounted perpendicular to each other. The frontal diagnostic quartz glass window of 85 mm in diameter (more than inner diameter of shock tube) was mounted in the end plate. The measurement section of the shock tube and the diagnostic are presented schematically in Fig. 1. The pressure has been controlled by PCB113B piezoelectric pressure gauge in the measurement section. During the experiment, the pressure did not change noticeably. The temperature evolution behind the reflected shock wave in the given experiments was not controlled. However, based on our previous measurements in 3% acetylene [13], we assumed that the temperature did not change significantly.

2.2. Extinction measurements

The extinction diagnostic is one of the most informative methods of investigation of the condensed phase formation process [4]. The beam of a conventional 20 mV HeNe laser was passed through two calcium fluoride windows of the shock tube (Fig. 1) and focused on the active photodiode PDA10A-ES (THORLABS) with a rise time of 10 ns. The detector was optically blocked by an interference filter of $\lambda = 632.8$ nm (FWHM 1 nm) to suppress the thermal radiation of the reacting gas-particle mixture. The experimental signals were registered by Tektronix TDS 2014B digital scope with 100 MHz band width. Particle extinction, determined by attenuation of passing radiation, is linked with the soot volume fraction by Lambert–Beer's law [4]. Due to uncertainties of optical properties of growing soot [21–23] in present study the "relative soot volume fraction" that is the product of volume fraction of condensed phase f_V and the function of refractive index of soot was chosen as