Shock Tube and Modeling Study of Soot Formation during Pyrolysis and Oxidation of Acetylene and Ethylene Mixtures

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1 Introduction

Acetylene plays a key role in soot formation. The pyrolysis and oxidation under fuel rich conditions of virtually all hydrocarbons leads to the formation of high concentrations of acetylene. The role of acetylene as a building material in the surface growth of soot particles has been recognized for a long time and is beyond doubt: acetylene is the main component in the surface growth of soot particles. Several experimental and modeling studies of soot formation during pyrolysis and oxidation of acetylene in shock waves have already been carried out [1–4]. An important intermediate in acetylene formation is ethylene, and therefore, the study of soot formation during the pyrolysis of this compound seems also relevant. Note that the pyrolysis of ethylene releases large amounts of hydrogen, which is known to suppress the process of soot formation. Therefore, a comparative experimental study of these two compounds is of undoubted interest for further improving the mechanism of soot formation. Additional information on the mechanism of soot formation can be obtained from experiments on the pyrolysis of these compounds in the presence of small additives of oxygen, which inhibits soot formation in several ways: through the conversion of hydrocarbon building material into deep oxidation products, very poor soot precursors, by suppressing the nucleation of soot particles, and through heterogeneous oxidation of soot precursors and soot particles.

2 Experimental

The experimental setup and procedure were described in detail elsewhere [5, 6]. Briefly, the experiments were performed in a stainless steel shock tube (inner diameter, 75 mm; driver section length, 1.5 m; driven section length, 3.2 m). The driven section was evacuated to 10^{-3} Torr. Air

leakage into the driven section did not exceed 10^{-4} Torr/min. Before each experiment, the driven section was purged twice with argon used for mixture preparation with intermediate pumping to 10^{-1} Torr.

The test mixtures were prepared manometrically and stored in lightproof containers. The components were acetylene (reagent grade), ethylene (reagent grade), and oxygen (99.0%). The diluent gas was argon (99.998%). In preparing the acetylene-containing mixtures, additional purification and chromatographic purity-control procedures were performed.

The soot yield and the temperature of the soot particles were determined by the two-beam absorption–emission method. The emission and absorption channel light beams passed through the same cross-section of the shock tube, perpendicular to each other. The measurements were carried out at a wavelength of 632.8 nm. The soot yield was defined in a conventional way: as the percentage of carbon bound in soot particles with respect to the total carbon present in the system. Since the soot particle size is much smaller than the probing light wavelength [7], the beam attenuation can be described with a high accuracy within the framework of the Rayleigh approximation.

Since there is a considerable discrepancies between the available values of E(m), we plotted the quantity $SY \times E(m)$ as a function of the time. Studying the formation of soot during the pyrolysis of toluene behind reflected shock waves, we estimated E(m) as 0.37, a value in close agreement with the most recent data [8, 9]: according to [8], E(m) = 0.373 and for the refractive index presented in [9] E(m) = 0.259. The quantity E(m) = 0.37 has the advantage that it was determined by us under conditions similar to those used in the present experiments.

Figures 1 and 2 shows typical absorption (frame 1) and emission (frame 2) signals. The emission signal intensity is given in relative units, in percent with respect to the signal intensity from the calibration band lamp.



Fig. 1. Typical time histories of the (1) absorption and (2) emission signals after the arrival of the reflected shock wave front at the observation cross section and of (3) the soot yield and (4) the soot particle temperature obtained from signals (1) and (2) for a mixture containing 5.0% acetylene in argon at various conditions behind the reflected shock wave: ACET81, $T_{50} = 1821$ K, $[M]_{50} = 2.36 \times 10^{-5}$ mol/cm³, $P_{50} = 3.53$ bar; ACET76, $T_{50} = 2049$ K, $[M]_{50} = 1.93 \times 10^{-5}$ mol/cm³, $P_{50} = 3.25$ bar; ACET79, $T_{50} = 2111$ K, $[M]_{50} = 2.32 \times 10^{-5}$ mol/cm, $P_{50} = 4.02$ bar. The probing light wavelength, $\lambda = 632.8$ nm. The symbols (triangles and squares) represent the calculated values of the soot yield and soot particle temperature, whereas the lines in panels 3 and 4 are the results of processing the absorption and emission signals, respectively.



Fig. 2. The same as in Fig. 1 for a mixture containing 5.0% acetylene + 1.5% oxygen in argon at the following conditions: ACET94, $T_{50} = 1617$ K, $[M]_{50} = 2.30 \times 10^{-5}$ mol/cm³, $P_{50} = 3.05$ bar; ACET96, $T_{50} = 1663$ K, $[M]_{50} = 2.34 \times 10^{-5}$ mol/cm³, $P_{50} = 3.19$ bar; ACET93, $T_{50} = 1835$ K, $[M]_{50} = 2.47 \times 10^{-5}$ mol/cm³, $P_{50} = 3.72$ бар.



Fig. 3. The same as in Fig. 1 for a mixture containing 5% ethylene in argon at the following conditions: ETHYL3, $T_{50} = 2318$ K, $[M]_{50} = 2.72 \times 10^{-5}$ mol/cm³, $P_{50} = 5.17$ bar; ETHYL5, $T_{50} = 2453$ K, $[M]_{50} = 2.69 \times 10^{-5}$ mol/cm³; $P_{50} = 5.41$ bar; ETHYL4, $T_{50} = 2545$ K, $[M]_{50} = 2.63 \times 10^{-5}$ mol/cm³, $P_{50} = 5.49$ bar.

Prior to the appearance of soot particles, the two-beam absorption-emission method provides only a noisy signal that makes it practically impossible to determine the soot particle temperature. After the

rarefaction wave arrives at the measurement cross section ($\sim 1200-1500 \ \mu s$), the emission signals begin to decrease markedly. This indicates a decrease in the mixture temperature in this cross section.

3 Kinetic model

The kinetic modeling was carried out using a reaction scheme of soot formation developed in [6] with some modifications in the gas phase kinetic mechanism and in the soot particle nucleation mechanism. These modifications were caused by obvious difference in the results of experiments and kinetic modeling of soot formation during the pyrolysis of various C_2H_2/Ar mixtures. At the same time, our preliminary calculations show that the modified kinetic model quantitatively reproduces the results of our experiments with a number of aliphatic and aromatic hydrocarbons (methane, ethylene, propane, propylene, benzene, and toluene).

Our kinetic model postulates that the soot precursors are PAHs formed by reactions between small saturated PAHs and PAH radicals or between PAH radicals only and between unsaturated polyyne-like aliphatic hydrocarbons. The reactions of formation of soot precursors are assumed to be irreversible. The reactions of surface growth can take place at active sites formed in reactions with hydrogen atoms. Thus, two different ensembles of soot precursors are considered in the model: soot precursors with and without active sites. Soot particles have a developed surface and each site on their surface can be activated and deactivated in the reactions with gas-phase species. At present, it is difficult to define an exact boundary between soot precursors and soot particles, but in the future, such a separation, at least formal, into several ensembles of particles may prove useful for improving the kinetic model.

The kinetic model of soot formation is based on a gas-phase reaction mechanism that describes the pyrolysis and oxidation of initial hydrocarbons, in particular ethylene and acetylene, and the formation and growth of PAHs through different reaction pathways up to coronene. The formation, growth, oxidation, and coagulation of soot precursors and soot particles were described using the discrete Galerkin technique [10].

The core of the gas-phase reaction mechanism is the reaction sequence of PAH formation in laminar premixed acetylene and ethylene flames (HACA). At the same time, the mechanism was extended to include a number of additional channels of PAH formation and growth (up to coronene) and a comprehensive set of reactions involving C_3 -, C_5 -, and C_7 -hydrocarbons. More specifically, the mechanism included (1) the alternating H-abstraction/ C_2H_2 -addition (HACA) route, resulting in the successive growth of PAHs; (2) the combination reactions of phenyl with C_6H_6 ; (3) the cyclopentadienyl recombination; and (4) the ring-closure reactions of aliphatic hydrocarbons. The principles underlying this mechanism are outlined in [6].

The modified gas-phase reaction mechanism was comprised of 3470 direct and reverse reactions between 298 different species, with the rate coefficients of some important reactions being pressure-dependent.

Soot precursors are formed by radical-molecule reactions of different PAHs, starting from phenylacetylene, acenapthalene, and ethynylnapthalene, up to coronene, by radical-radical reactions (from cyclopentaphenanthrene up to coronene radicals), and by combination reactions of unsaturated polyyne-like aliphatic hydrocarbons. These reactions result in the formation of polyaromatic molecules containing from 16 to 48 carbon atoms, which are stabilized by the formation of the new chemical bonds. Soot precursors are activated in reactions with H and OH radicals and deactivated in reactions with H, H₂ and H₂O. Soot precursors grow via reactions with C_2H_2 , C_4H_2 , and C_6H_2 (the concentrations of which are rather high in the pyrolysis and oxidation of aliphatic and aromatic hydrocarbons), reactions with polyaromatic molecules and radicals, and the process of coagulation. Soot precursors are oxidized by O and OH radicals. They are transformed into soot particles through internal conversion reactions, in which the number of active sites in the reacting system is preserved. Soot particles grow in the reactions with C_2H_2 , C_4H_2 and R_4 has through internal conversion reactions with C_2H_2 , C_4H_2 , C_6H_2 and PAH molecules and radicals. All the types of soot particles were postulated to participate in coagulation.

4 Results and discussion

The experimentally measured and calculated temperature dependences of the soot yield in the pyrolysis and oxidation of different C_2H_2/Ar , C_2H_4/Ar , $C_2H_2/O_2/Ar$ and $C_2H_4/O_2/Ar$ mixtures and dependence of the temperature of soot particles formed during the pyrolysis and oxidation of C_2H_2/Ar , $C_2H_2/O_2/Ar$, and $C_2H_2/C_3H_6O/Ar$ mixtures on the calculated initial temperature behind the reflected shock wave are shown in Figs. 4 and 5.



Fig. 4. Measured and calculated temperature dependences of the soot yield for the pyrolysis of three different acetylene/Ar mixtures behind reflected shock waves (left) and dependence of the temperature of soot particles formed during the pyrolysis and oxidation of acetylene/Ar mixtures for a reaction time of $\tau_{\text{react}} = 1.0$ ms on the calculated initial temperature behind the reflected shock wave (right). The left plot: (\blacksquare) 5% C₂H₂ in argon, (\bullet) 3% C₂H₂ in argon, and (∇) 1.5% C₂H₂ in argon ($P_{50} = 3.0-4.5$ bar, E(m) = 0.37, $\tau_{\text{react}} = 1.5$ ms). The closed and open symbols represent, respectively, the measured and calculated values; the lines are the results of log-normal approximation of the experimental data. The right plot: the composition of the test mixture is given in the figure (C₃H₆O – acetone).



Fig. 5. Measured (closed symbols) and calculated (open) temperature dependences of the soot particle yield for the pyrolysis of three different ethylene/Ar mixtures (left) and a 5% ethylene + 1.5% oxygen + argon mixture (right) behind the reflected shock waves. The left plot: (\blacksquare) 5% C₂H₄ in argon, (\blacktriangle) 3% C₂H₄ in argon, (\blacklozenge) 1.5% C₂H₄ in argon. The right plot: (\blacksquare) 5% C₂H₄ + 1.5% O₂ in Ar. P₅₀ = 3.0–5.5 bar, E(m) = 0.37, $\tau_{react} = 1.5$ ms. The lines are the results of log-normal approximation of the experimental data.

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The novel kinetic model closely describes the temperature dependences of the soot yield at the different initial concentration of acetylene and ethylene in the test mixture over the entire temperature range. As can be seen from Fig. 3, exothermic effect was observed only in some separate experiments with a $5.0\%C_2H_2/Ar$ mixture and in all experiments with a $5.0\%C_2H_2/1.5\%O_2/Ar$ mixture. For all other mixtures, presented in Fig. 3, only endothermic effect is observed, increasing with the temperature. Given the uncertainty in temperature measurements of ~50–100 K, these results are in satisfactory agreement with the recent experimental data presented in [4].

5 Conclusions

The experiments on the pyrolysis and oxidation under fuel rich conditions of C_2H_2/Ar , $C_2H_2/O_2/Ar$, C_2H_4/Ar , and $C_2H_4/O_2/Ar$ mixtures behind reflected shock waves were performed. The soot yield and the soot particle temperature were determined using the double-beam absorption-emission technique. The kinetic modeling was carried out using a reaction scheme of soot formation developed in [6] with some modifications in the gas phase and soot particle nucleation kinetic mechanisms. The measured and calculated temperature and soot yield profiles, as well as the temperature dependences of the soot yield obtained for the conditions behind reflected shock waves ($T_{50} = 1400-2850$ K, $P_{50} = 2.5-5.5$ bar) during pyrolysis and oxidation under fuel rich conditions of C_2H_2/Ar , $C_2H_2/O_2/Ar$, C_2H_4/Ar , and $C_2H_4/O_2/Ar$ mixtures, were demonstrated to be in good agreement.

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References

[1] Frenklach M, Ramachandra MK, Matula RA. (1984). Soot formation in shock tube oxidation of hydrocarbons. Proc. Combust. Inst. 20:871.

[2] Knorre VGg, Tanke D, Thienel Th, Wagner HGg. (1996) Soot formation in the pyrolysis of benzene/acetylene and acetylene/hydrogen mixtures at high carbon concentrations. Proc. Combust. Inst. 26:2303.

[3] Vlasov PA, Warnatz J, (2002). Detailed kinetic modeling of soot formation in hydrocarbon pyrolysis behind shock waves. Proc. Combust. Inst. 29: 2335.

[4] Eremin A, Gurentsov E, Mikheyeva E. (2012). Experimental study of molecular hydrogen influence on carbon particle growth in acetylene pyrolysis behind shock waves. Combust. Flame. 159: 3607.

[5] Agafonov GL, Smirnov VN, Vlasov PA. (2010). Shock tube and modeling study of soot formation during pyrolysis of propane, propane/toluene and rich propane/oxygen mixtures. Combustion Science and Technology. 182: 1645.

[6] Agafonov GL, Smirnov VN, Vlasov PA. (2011). Shock tube and modeling study of soot formation during the pyrolysis and oxidation of a number of aliphatic and aromatic hydrocarbons. Proc. Combust. Inst. 33: 625.

[7] Haynes BS, Wagner HG. (1981). Soot formation. Prog. Energy Combust. Sci. 7(4): 229.

[8] Williams TC, Shaddix CR, Jensen KA, Suo-Anttila JM. (2007). Measurement of the dimensionless extinction coefficient of soot within laminar diffusion flames. Int. J. Heat and Mass Transfer. 50:1616.

[9] Smyth KC, Shaddix CR. (1996). The elusive history of m = 1.57 - 0.56i for the refractive index of soot. Combust. Flame. 107:314.

[10] Deuflhard P, Wulkow M. (1989). Computational treatment of polyreaction kinetics by orthogonal polynomials of a discrete variable. Impact of Computing in Science and Engineering. 1: 269.