

# Detailed Kinetic Modeling of Soot Formation during Shock Tube Pyrolysis of C<sub>6</sub>H<sub>6</sub>: Direct Comparison with the Results of Time-Resolved Laser-Induced Incandescence (LII) and CW-Laser Extinction Measurements

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In practical combustion devices such as industrial furnaces, gas turbines, or internal combustion engines, in which hydrocarbons are used as a fuel, very frequently, the real combustion occurs under fuel rich conditions. As a result, soot is formed as a by-product in the region where the local concentration of oxygen is not sufficient to convert the fuel into water and carbon dioxide. Since this soot emission causes various design problems for practical combustors, the severe environmental damages and human health problems, there is a need for better understanding of the processes that are responsible for the formation and oxidation of soot. In spite of the fact that intensive studies of soot formation have been performed over the last three decades, understanding of the kinetic mechanism of soot formation still remains a challenging problem of combustion science. This is caused by several reasons: by the complexity of the chemical kinetics of polyaromatic hydrocarbon (PAH) formation, growth, coagulation, and by the numerical problems of incorporation of heterogeneous reactions into large gas phase kinetic schemes. Soot formation process was mainly studied in laminar flames, but many studies have also been performed using the shock tube technique, which presents the advantage of a homogeneous reactor and gives the possibility to measure soot formation under known temperature, pressure, mixture composition, and observation time, which, usually, is limited to a few milliseconds.

Recently, a new detailed kinetic model of soot formation in hydrocarbon pyrolysis under conditions typical for shock tube experiments was developed [1]. It combines the mechanism of formation of polyaromatic hydrocarbons, polyne and HACA (H-abstraction-C<sub>2</sub>H<sub>2</sub>-addition) pathways of soot formation, and the mechanisms of acetylene pyrolysis and pure carbon cluster formation. The kinetic model developed consists of

approximately 1700 gas-phase elementary reactions between 141 different species, where the rate coefficients of some important reactions have pressure dependence, and a set of reactions with participation of heterogeneous particles, i.e., soot precursors and soot particles formed from the gas-phase species through the HACA and polyynes pathways. The gas-phase reaction mechanism includes a complete set of the PAH formation reactions developed in [2] for laminar premixed acetylene and ethylene flames with all modifications presented in [3], in combination with the reaction mechanisms of acetylene pyrolysis [4,5], the mechanism of formation of polyyne molecules [6,7], and a set of the gas-phase reactions of the formation of small pure carbon clusters up to  $C_{30}$  [8]. The formation, growth and coagulation of soot precursors and soot particles are described within the framework of a discrete Galerkin technique suggested by Deuflhard and Wulkow [9] for the solution of ordinary differential equations arising from heterogeneous polymerization kinetics. The method is based on an error-controlled expansion of the size distribution function of polymer species into the orthogonal polynomials of a discrete variable, in particular, the chain length or number of monomers in the polymer particle. This approach makes it possible to preserve a discrete character of any elementary transformations of heterogeneous particles and to describe them as elementary chemical reactions for the heterogeneous particles of all sizes. The heterogeneous particles can also react with the gas-phase species, and, thus, a connection with the gas-phase chemistry of soot particles is provided during the whole calculation. The kinetic model was tested for various aliphatic and aromatic hydrocarbons and their mixtures and showed the role of the polyyne and HACA pathways of soot formation under various conditions for different hydrocarbons.

Laser-based diagnostics provide powerful and unique capabilities for non-intrusive measurements in reactive flows. CW-laser extinction is a line-of-sight method, typically employing continuous wave (CW) laser sources, fixed or variable in wavelength. This method is widely used to determine the soot yield, induction time, and the observable rate of surface growth of soot particles. At the same time, by this method, it is practically impossible to measure the sizes of fine soot particles of a few nanometers in diameter. Laser induced incandescence (LII) is an alternative optical technique which allows particle sizing down to a few nanometers. It is based on a fast particle temperature increase by absorption of a short laser pulse and on the observation of the subsequent time dependent thermal radiation, which depends on the particle temperature. As the particles are cooled mainly through heat transfer to the carrier gas, larger particles (with a larger volume-to-surface ratio) need longer times to cool down than smaller ones. Under particular assumptions concerning the size distribution of the primary soot particles, one can determine the mean size of the soot particles from the measurements of the rate of

cooling (actually, the spectral radiation) of the ensemble of soot particles. The combination of the cw-laser extinction and time-resolved LII methods provides information, which is important to verify theoretical models of soot formation.

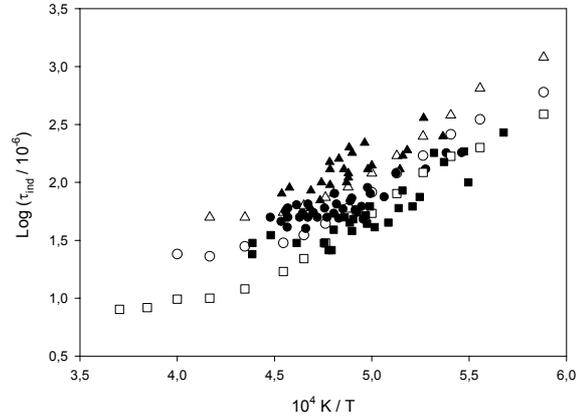
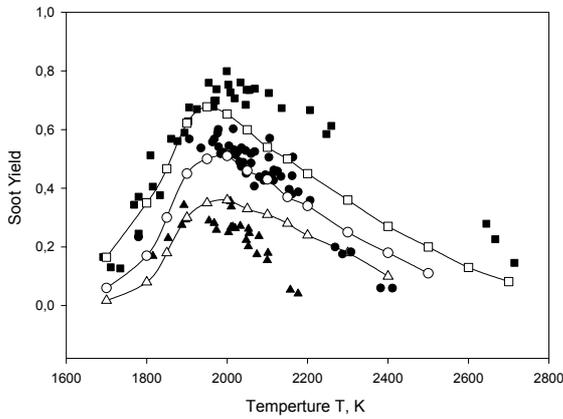


Fig. 1. The temperature dependences of the experimentally measured (closed symbols) and calculated (open symbols) soot yield for a fixed reaction time of  $t_r = 1300 \mu\text{s}$  and pressure  $p = 1.2 \text{ bar}$  for different benzene concentrations in the reactive mixture: ( $\square$ ) 2%  $\text{C}_6\text{H}_6$ , ( $\circ$ ) 1%  $\text{C}_6\text{H}_6$ , and ( $\triangle$ ) 0.5%  $\text{C}_6\text{H}_6$  in Ar.

Fig. 2. Experimentally measured (closed symbols) and calculated (open symbols) values of the induction time of soot particle formation for different benzene concentrations in the reactive mixture versus inverse temperature: ( $\square$ ) 2%  $\text{C}_6\text{H}_6$ , ( $\circ$ ) 1%  $\text{C}_6\text{H}_6$ , and ( $\triangle$ ) 0.5%  $\text{C}_6\text{H}_6$  in Ar,  $p = 1.2 \text{ bar}$ .

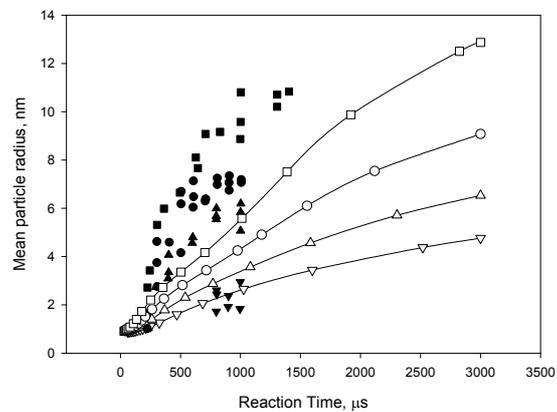
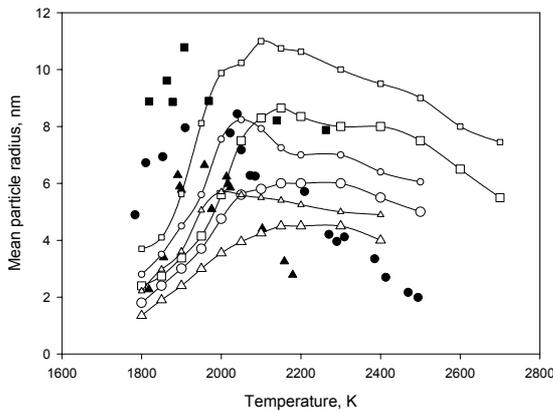


Fig. 3. The temperature dependences of the experimentally measured (closed symbols) and calculated (open symbols) values of the mean soot particle radius for a fixed reaction time of  $t_r = 1000 \mu\text{s}$  (small open symbols correspond to  $t_r = 2000 \mu\text{s}$ ) for different benzene concentrations in the reactive mixture: ( $\square$ ) 2%  $\text{C}_6\text{H}_6$ , ( $\circ$ ) 1%  $\text{C}_6\text{H}_6$ , and ( $\triangle$ ) 0.5%  $\text{C}_6\text{H}_6$  in Ar,  $p = 1.2 \text{ bar}$ .

Fig. 4. Experimentally measured (closed symbols) and calculated (open symbols) values of the mean soot particle radius for different benzene concentrations in the reactive mixture versus reaction time: ( $\square$ ) 2%  $\text{C}_6\text{H}_6$ , ( $\circ$ ) 1%  $\text{C}_6\text{H}_6$ , ( $\triangle$ ) 0.5%  $\text{C}_6\text{H}_6$ , and ( $\nabla$ ) 0.25%  $\text{C}_6\text{H}_6$  in Ar,  $p = 1.2 \text{ bar}$ ,  $T = 2000 \text{ K}$ .

The main goal of the present study is a direct comparison of the results of experimental measurements of the soot yield and induction time measured by the cw-laser extinction technique, and the mean radius of soot particles determined by the time-resolved laser-induced incandescence method during C<sub>6</sub>H<sub>6</sub> pyrolysis behind reflected shock waves [10] with the results of calculations of these values with the use of the detailed kinetic model of soot formation developed in [1]. The main results of this comparison are presented in Figs. 1—4. The analysis of the influence of various factors connected with the detailed kinetic model of soot formation and experimental technique used in the shock tube measurements (the time-resolved LII and cw-laser extinction measurements) on the main parameters of soot formation (the soot yield, induction time, and mean radius of soot particles) showed that the nucleation and surface growth rates of the HACA pathway of soot formation, the size distribution of soot particles, as well as the accommodation coefficient, the geometry dependent heat transfer coefficient and the refractive index of soot particles are most important to provide a quantitative agreement between the experimentally measured and calculated parameters of soot formation.

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