

# Detailed Kinetic Modeling of Soot Formation in Pyrolysis of Benzene/Acetylene/Argon Mixtures

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## Abstract

A detailed kinetic model of soot formation in hydrocarbon pyrolysis [1] and oxidation [2] under conditions typical for shock tube experiments was tested for soot formation modeling of benzene/argon, acetylene/argon, and various benzene/acetylene/argon mixtures. The results from the simulations and the reaction flow analysis showed the role of polyynes and HACA (H-abstraction-C<sub>2</sub>H<sub>2</sub>-addition) pathways of soot formation. The model considered can reproduce the main parameters of soot formation. All the numerical results were calculated while keeping the entire set of the model parameters fixed.

## Introduction

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) and soot precursor formation, by particular difficulties of the kinetic description of the soot particles' surface growth, and by the numerical problems of the incorporating heterogeneous reactions into large gas phase kinetic schemes.

## Specific Objectives

A detailed kinetic model of soot formation by means of a suitable numerical technique (Discrete Galerkin Method, [3]) was applied for simulating the processes of soot formation in shock tube experiments. The kinetic model had to describe soot formation processes in pyrolysis and oxidation of different hydrocarbons and their mixtures.

## Results and Discussion

A detailed kinetic modelling of soot formation process in pyrolysis and oxidation of different hydrocarbons and their mixtures was carried out. The model used was particularly described in [1,2]. Soot precursors are formed through a combine scheme of the well-known H-abstraction/C<sub>2</sub>H<sub>2</sub>-addition (HACA) pathway and the polyynes pathway. Soot formation, growth and coagulation of the soot particles are described by means of a discrete Galerkin method suggested by Deuflhard and Wulkow [3] for the simulation of macromolecular and standard chemical reactions. The program was slightly modified and expanded to cope with several specific polymerisation steps [4].

In order to validate the ability of the detailed kinetic model to describe soot formation in pyrolysis of

hydrocarbon mixtures an expanded study of benzene/acetylene mixtures has been performed. Usually, several parameters of soot formation process such as the induction time  $\tau$ , the soot growth rate constant  $k_f$ , and the soot yield  $SY$  are measured in the experiments. They are known to be very sensitive to the chemical structure of the hydrocarbon pyrolyzed. The induction time  $\tau$  (s) is defined as the intersection point of the tangent at the inflection point of the soot yield curve with the time axis. The soot yield  $SY$  is defined as the ratio of carbon finally concentrated in soot particles to the total carbon content in the parent mixture. The soot yield profiles after the inflection point can be approximated by an empirically obtained first order rate law, where the parameter  $k_f$  (s<sup>-1</sup>) is the soot growth rate constant, which can be interpreted as an effective measure of the "active lifetime" of soot particles, assuming that they are losing their reactivity.

Arrhenius type plots of the experimentally measured [5] and calculated values of the induction time  $\tau$  at a pressure of 60 bar are presented in Fig. 1 for acetylene, benzene, and various benzene/acetylene mixtures with different carbon atom concentrations. One can observe a good agreement between the experimentally measured and calculated values of the induction time for a pure benzene/Ar mixture, a satisfactory agreement for a pure acetylene/Ar mixture, and a particular discrepancy for the benzene/acetylene/Ar mixtures. The induction times determined experimentally in the work [5] for different benzene/acetylene/argon mixtures are between those for the pure hydrocarbons. The calculated values of  $\tau$  for various benzene/acetylene/argon mixtures are smaller than those for a benzene/Ar mixture.

The soot formation starts much earlier in benzene pyrolysis when the PAH route [6,7] of soot formation dominates: some benzene molecules are decomposed with the formation of small aliphatic compounds, which form C<sub>2</sub>H<sub>2</sub> molecules. Then, they participate in further growth of PAH molecules, which, in turn, form soot

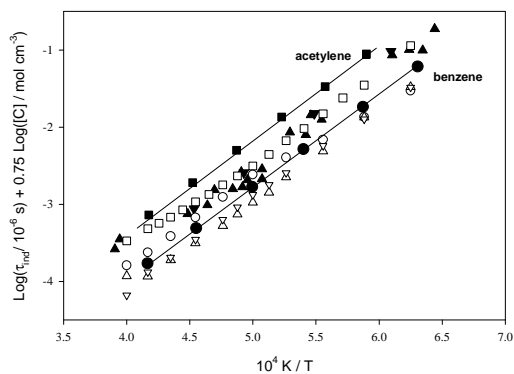
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precursors and provide the major contribution into the surface growth of soot particles. In acetylene pyrolysis, the polyne pathway [8,9, and 10] of soot formation dominates.

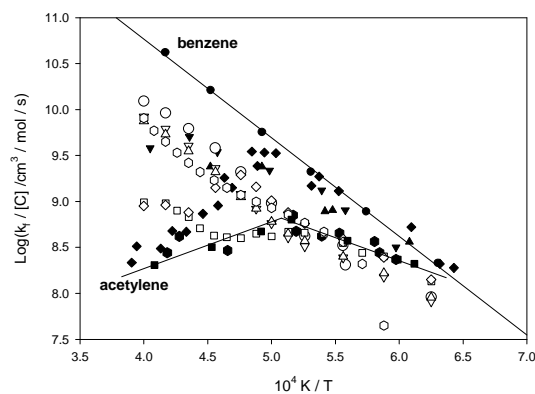


**Fig. 1:** Arrhenius type plot of the normalized induction time ( $\tau \cdot [C]^{0.75}$ ) for mixtures with various benzene/acetylene ratios (B/A) and carbon atom concentrations at a pressure of 60 bar: (squares) pure acetylene,  $[C] = 4 \cdot 10^{-6} \text{ mol/cm}^3$ , (circles) pure benzene,  $[C] = 4 \cdot 10^{-6} \text{ mol/cm}^3$ , (triangles) B/A = 1/1,  $[C] = 5 \cdot 10^{-6} \text{ mol/cm}^3$ , (triangles inverted) B/A = 2.5/1,  $[C] = 12 \cdot 10^{-6} \text{ mol/cm}^3$ . Open symbols designate the results of calculations, closed symbols the experimental results.

The precursors of soot particles are formed in reactions of polymerization of higher polyynes ( $C_8H_2$ ,  $C_{10}H_2$ , and  $C_{12}H_2$ ), and  $C_2H_2$ ,  $C_4H_2$  and  $C_6H_2$ , which provide the major contribution into the surface growth of soot particles. The reaction flow analysis showed that in this case the first aromatic ring is formed mostly through combination reaction of two propargyl radicals. Nevertheless, in case of acetylene pyrolysis, without additional channels of formation of PAH molecules, the PAH route based only on the HACA mechanism proposed in [6,7] cannot compete with the polyne pathway. Similar slopes of the temperature dependences of the induction times of soot formation in benzene and acetylene pyrolysis can be explained by the fact that  $C_2H_2$  molecules and  $C_2H$  radical are the key species both in the HACA route of PAH growth and in the formation of polyne molecules. The  $C_2H_2$  additive facilitates a further growth of PAH compounds via the HACA route in the gas phase. As a result, the calculated induction times for benzene/acetylene/Ar mixtures are even smaller than those for a pure benzene/Ar mixture. The pressure dependence of the induction time of soot formation was not found in the experiments and in our calculations. The calculations also show the importance of the surface growth reactions with participation of pyrene, phenanthrene, and biphenyl molecules and pyrene and phenanthrene radicals (PAH route) in the model.

The experimentally measured [5] and calculated temperature dependences of the normalized soot growth rate constant ( $k_f/[C]$ ) at a pressure of 60 bar are

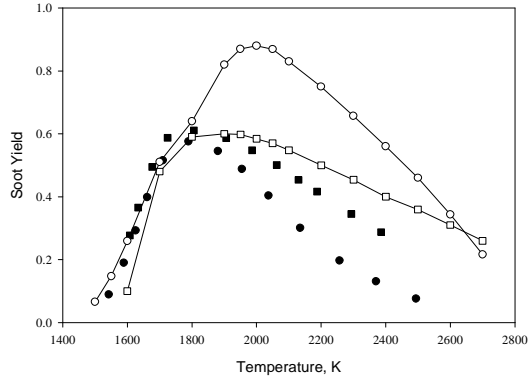
presented in Fig. 2 for benzene, acetylene, benzene/acetylene, and acetylene hydrogen mixtures.



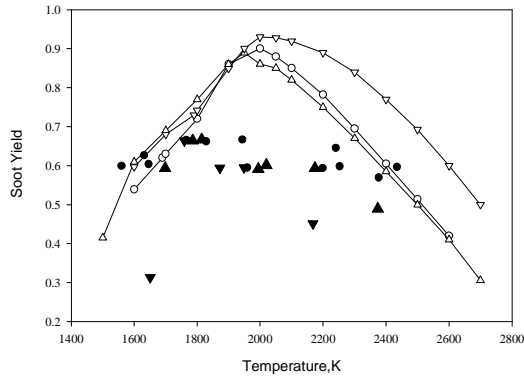
**Fig. 2:** Temperature dependences of the normalized observable rate of soot particle growth ( $k_f/[C]$ ) for benzene, acetylene, benzene/acetylene, and acetylene hydrogen mixtures at a pressure of 60 bar: (squares) pure acetylene,  $[C] = 4 \cdot 10^{-6} \text{ mol/cm}^3$ , (circles) pure benzene,  $[C] = 4 \cdot 10^{-6} \text{ mol/cm}^3$ , (triangles inverted) B/A = 10/1,  $[C] = 9 \cdot 10^{-6} \text{ mol/cm}^3$ , (diamonds) B/A = 1/1,  $[C] = 5 \cdot 10^{-6} \text{ mol/cm}^3$ , (triangles) B/A = 2.5/1,  $[C] = 12 \cdot 10^{-6} \text{ mol/cm}^3$ , (hexagones)  $C_2H_2/H_2 = 1/1$ ,  $[C] = 2 \cdot 10^{-6} \text{ mol/cm}^3$ . Open symbols designate the results of calculations, closed symbols the experimental results. Solid lines are the best fits for pure benzene (upper curve) and pure acetylene (lower curve).

The model properly describes a pronounced difference of  $k_f$  values for benzene ( $k_f = 49885$  for  $T = 2500 \text{ K}$ ,  $p = 60 \text{ bar}$ ,  $[C] = 4 \cdot 10^{-6} \text{ mol/cm}^3$ ) and acetylene ( $k_f = 3896$  for  $T = 2500 \text{ K}$ ,  $p = 60 \text{ bar}$ ,  $[C] = 4 \cdot 10^{-6} \text{ mol/cm}^3$ ) pyrolysis at high temperatures but cannot describe a sharp decrease of the  $k_f$  values for pure acetylene and some benzene/acetylene mixtures at high temperatures. This means that actually soot particles very rapidly become inactive with respect to the surface growth at high temperatures when the concentration of acetylene in the gas phase is still considerably high. In this case, the model overestimates the soot yield and  $k_f$  values.

The experimentally measured [5] and calculated temperature dependences of the soot yield in pyrolysis of benzene, acetylene, and benzene/acetylene mixtures are presented in Fig. 3 and Fig. 4. The model overestimates the soot yield for benzene (Fig. 3) and benzene/acetylene mixtures (Fig. 4) at high temperatures but describes properly the bell-shaped temperature dependence of the soot yield and soot yield for acetylene/argon mixture. The model predicts properly the induction time for pure benzene/Ar mixtures but considerably overestimates the results for the soot yield as well as shifts the maximal temperature range for the soot yield with almost 200 K. On the other hand the calculated values of  $\tau$  in acetylene pyrolysis differ from the experimental while, the calculated soot yield correspond to the experimentally obtained.



**Fig. 3:** Temperature dependences of the soot yield in the pyrolysis of benzene/Ar and acetylene/Ar mixtures at a pressure of 6 bar: (squares) pure acetylene,  $[C] = 4 \cdot 10^{-6}$  mol/cm<sup>3</sup>, (circles) pure benzene,  $[C] = 4 \cdot 10^{-6}$  mol/cm<sup>3</sup>. Open symbols and lines designate the results of calculations, closed symbols the experimental results.



**Fig. 4:** Temperature dependences of the soot yield in the pyrolysis of benzene/acetylene/Ar mixtures at a pressure of 6 bar: (triangles) B/A = 1/2.5,  $[C] = 6 \cdot 10^{-6}$  mol/cm<sup>3</sup>, (circles) B/A = 1/1,  $[C] = 5 \cdot 10^{-6}$  mol/cm<sup>3</sup>, (triangles inverted) B/A = 2.5/1,  $[C] = 9 \cdot 10^{-6}$  mol/cm<sup>3</sup>. Open symbols and lines designate the results of calculations, closed symbols the experimental results.

Some of the possible reasons for these disagreements are discussed above. The both submodels (PAH and polyne) are based on the formation and growth of C<sub>2</sub>H<sub>2</sub> and higher hydrocarbons with even number of carbon atoms. One of the main products of the gas phase species in case of benzene pyrolysis is C<sub>2</sub>H<sub>2</sub>. On the other hand C<sub>2</sub>H<sub>2</sub> molecules and C<sub>2</sub>H radicals play a key role in the process of polyne growth. Besides, C<sub>2</sub>H<sub>2</sub> molecules participate in the HACA pathway of PAHs growth as well as in soot surface growth due to the both sub-models (PAH and polyne). Other authors like [Marinov, Rasmussen] propose soot formation models in which the gas phase chemistry is based mostly on pathways with odd-carbon-atom species.

Another possible reason could be the inconsistent choice or the incomplete knowledge of the reaction kinetics and thermodynamics of some of the key species presented in the gas phase. All calculations are made, while keeping the entire set of chemical reactions and thermo-chemical data fixed for all kinds of reaction systems studied. We hope that future efforts in these directions will improve the incorporation of these reaction pathways in a consistent and systematic manner.

**Table 1:** Induction time, soot yield, number density and soot particle diameter calculated at  $T = 1800$  K and  $p = 6.4$  bar for acetylene/Ar, benzene/Ar, and benzene/acetylene/Ar (B/A) mixtures at a reaction time of 1.7 ms and carbon atom concentration of  $[C] = 6 \cdot 10^{-6}$  mol/cm<sup>3</sup>:

Mixture Composition	Ind.Time, $\mu$ s	Soot Yield	Nsoot, cm <sup>-3</sup>	$\langle d \rangle_{\text{soot}}$ , nm
acetylene	162.44	0.599	2.69E+13	22.64
B/A=1/20	125.80	0.691	6.70E+13	20.07
B/A=1/10	96.76	0.759	5.90E+13	18.30
B/A=1/6	77.88	0.788	1.17E+14	17.31
B/A=1/4	65.47	0.790	1.05E+14	16.05
B/A=1/1	51.13	0.719	2.57E+14	11.58
B/A=4/1	43.56	0.695	3.83E+14	9.98
B/A=6/1	46.79	0.690	3.90E+14	9.75
B/A=10/1	52.24	0.704	4.04E+14	9.61
B/A=20/1	55.75	0.699	4.09E+14	9.53
benzene	80.80	0.650	3.30E+14	8.40

The induction time, soot yield, number density, and the soot particle diameter calculated at  $T = 1800$  K and  $p = 6.4$  bar for pyrolysis of benzene/Ar, acetylene/Ar, and various benzene/acetylene/Ar mixtures are presented in Table 1. The calculated induction time for benzene pyrolysis ( $\tau_{\text{ind}} = 80.80$   $\mu$ s) is shorter by a factor of two than the induction time for acetylene pyrolysis ( $\tau_{\text{ind}} = 162.44$   $\mu$ s). The addition of small amount of acetylene into benzene mixture results in an essential reduction of the induction time, where for a mixture of B/A = 20/1,  $\tau_{\text{ind}} = 55.75$   $\mu$ s. The shortest induction time was calculated for a benzene/acetylene mixture in correlation 4/1:  $\tau_{\text{ind}} = 43.56$   $\mu$ s. Further increase of the acetylene fraction into the benzene/acetylene mixture results in an increase of the induction time from  $\tau_{\text{ind}} = 51.13$   $\mu$ s for B/A = 1/1 up to  $\tau_{\text{ind}} = 125.80$   $\mu$ s for B/A = 1/20. Note that, the induction times determined experimentally in the work [5] for different benzene/acetylene/argon mixtures are between those for the pure hydrocarbons at 60 bar.

The mean diameter and concentration of the soot particles calculated for the listed mixtures at the same working conditions vary from their maximal value for the  $\langle d \rangle = 22.64$  nm, and minimal value for the  $n_{\text{soot}} = 2.69 \cdot 10^{13}$  cm<sup>-3</sup> for pure acetylene/Ar mixture, through  $\langle d \rangle = 11.58$  nm, and  $n_{\text{soot}} = 2.57 \cdot 10^{14}$  cm<sup>-3</sup> for a B/A =

1/1 mixture, and further up to their minimal value for the  $\langle d \rangle = 8.40$  nm, and maximal value for the  $n_{\text{soot}} = 3.3 \cdot 10^{14} \text{cm}^{-3}$  for pure benzene/Ar mixture. Under these conditions, the maximal soot yield is observed for B/A = 1/4 mixture ( $SY = 0.79$ ), and for all mixture compositions the soot yield is higher than for a pure acetylene/argon mixture ( $SY = 0.599$ ) and benzene/argon mixture ( $SY = 0.65$ ).

### Conclusions

A detailed kinetic modelling of soot formation in pyrolysis of benzene/Ar, acetylene/Ar, and benzene/acetylene/Ar mixtures is carried. The results of calculations are compared with the results of the experimentally measured values for the induction time, observable rate of soot particle growth and the soot yield for the enumerated mixtures behind reflected shock waves.

The calculations confirmed a remarkably non-linear effect of acetylene additives into benzene/Ar mixtures. The addition of acetylene to benzene results in a decrease of the induction time for all mixture compositions investigated. The concentration of soot particles and soot precursors decreases steadily from its maximal value for a pure benzene/Ar mixture to its minimal value for a pure acetylene/Ar mixture.

The model does not demonstrate a pronounced pressure dependence of the soot yield but shows an essential dependence of the soot yield, as well as the induction time and  $k_f$ , on the concentration of carbon atoms in the mixture.

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