An experimental and simulation study of the effect of acetone and propane additives on soot formation in acetylene pyrolysis behind reflected shock waves

G L Agafonov1, P A Vlasov1,2, V N Smirnov1, A M Tereza1, A A Garmash2 and V V Shumova1,3

1 Semenov Institute of Chemical Physics of the Russian Academy of Sciences, Kosygina 4, Moscow 119991, Russia
2 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe Shosse 31, Moscow 115409, Russia
3 Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia

E-mail: iz@chph.ras.ru

Abstract. Experimental investigations and detailed kinetic simulations of the formation of soot particles during pyrolysis of mixtures of acetylene with acetone and propane behind reflected shock waves are performed. Acetone and propane additives are found to substantially promote the process of soot formation as compared with that in acetylene–argon mixtures. Detailed kinetic simulations closely reproduce our own experimental results and published data. The kinetic model of soot formation is comprised of 4782 direct and reverse reactions involving 372 species. The predictive possibility of the kinetic model of soot formation is tested by describing the effect of acetone and propane additives to acetylene–argon mixtures on soot formation. All the kinetic parameters of the unified kinetic model are kept constant. The indicated additives enhance the soot yield because polyyne-dominated pathway of soot nucleation, characteristic of unseeded acetylene–argon mixtures, is augmented by the aromatic pathway, typical of most hydrocarbons.

1. Introduction

Soot formation is a very complex phenomenon [1]. Although, in the last few decades, significant progress has been made regarding the main chemical species and detailed reaction pathways involved in the formation of polycyclic aromatic hydrocarbons (PAHs), nascent soot particles, and their subsequent surface growth, certain key steps of these processes remain understood poorly [2].

Soot particles in exhaust gases from combustion plants have become a major concern, affecting both the environment and human health. Increasingly strict regulations on the emissions of particulate matter (PM) are enacted. It is believed that the main component of PM produced in the combustion of hydrocarbon fuels is soot, which is formed in the following pyrolytic and oxidative steps: the formation of radical precursors, such as polyynes and PAHs through radical reactions of small molecules and (or) their fragments, molecular growth, nucleation, coagulation, and oxidation [2–6]. Although the process of soot formation has been extensively investigated both experimentally and theoretically in a huge number of investigations, some issues need to be
addressed, in particular, the chemical characteristics of compounds formed in flames and shock waves during soot inception [7, 8].

While soot formation in the combustion of individual fuels has been studied extensively, the formation of soot from fuel mixtures has been the subject of a limited number of works. There is conflicting experimental evidence on the occurrence of synergistic effects in the sooting propensity of binary fuel mixtures of various compositions, as well as different interpretations of such effects [9, 10]. In this context, the synergistic effect is defined as the increase in the soot yield of the mixture over the sum of the contributions from the individual components.

Frenklach et al [11] observed the synergistic effect for many mixtures and concluded that the effect could be explained by considering the acetylene based inception and growth mechanisms.

Hwang et al [12] tested various ethylene–propane mixtures to elucidate whether odd-carbon numbered species could contribute to the synergistic effect. The authors interpreted the manifestation of the synergistic effect in the concentrations of PAHs and soot particles as an evidence that the traditional role of acetylene in the formation of a first aromatic ring and in the growth of soot particles may not be solely responsible for this effect and suggested that odd-carbon-number species, in particular propargyl (C\textsubscript{3}H\textsubscript{3}), may play a certain role. It was also supposed that methyl radicals could contribute to the synergistic effect by being involved in the formation of propargyl.

In addition to being of interest for soot formation control, studying the effect of various hydrocarbon additives, such as acetylene and benzene, on soot formation is also a promising way to probe into the mechanisms of the formation of first aromatic rings and soot particle nuclei and (or) to assess the relative contributions of the different pathways to the formation of PAHs and soot [13].

In particular, a pronounced promoting effect of toluene additives on soot formation during propane pyrolysis in a shock tube was observed in [14].

The mechanism of soot inception remains largely unclear, in particular the chemical nature of soot precursors [15]. This motivated the present study aimed at obtaining further insights into the chemistry of soot precursors in the shock-tube pyrolysis of acetylene, acetylene–acetone and acetylene–propane mixtures.

The most important step of the overall process of soot formation is the nucleation of soot particles. The following two alternative nucleation pathways are usually considered: polyynic (polyacetylenic) and polyaromatic. The molecules of polyynes, polyyne-like, and polyaromatic hydrocarbons have a high thermal stability [16] and, therefore, do not decompose at high temperatures typical of soot formation, although they may participate in the nucleation and surface growth processes.

The role of acetylene molecules in soot formation has been discussed for a long time, and it is believed now that acetylene is the main species involved in the process of surface growth of soot particles [4]. Acetylene is also the main active component in the HACA mechanism [4] (HACA: hydrogen abstraction–acetylene addition): it ensures the sequential growth of polyaromatic molecules through the abstraction of hydrogen atom with the formation of active sites followed by the addition of acetylene molecules from the gas phase to these active sites. As we know, the very first direct experimental evidence for the validity of the HACA mechanism, which so far had only been speculated theoretically, is reported in [17].

In recent years, the majority of researches has focused almost exclusively on the polyaromatic pathway of soot nucleation. Such models qualitatively, in some cases quantitatively, describe the main parameters of the process of soot formation in the pyrolysis and oxidation of most hydrocarbons (both aliphatic and aromatic). In a number of our studies [14, 18–21], the developed kinetic model of soot formation enabled to quantitatively describe the process for a variety of hydrocarbons, such as methane, propane, propylene, ethane, acetone, ethanol, benzene, toluene, and ethylbenzene, at fixed set of kinetic parameters.
However, our attempts to apply this model to soot formation in the pyrolysis of acetylene showed that the theoretically calculated maximum in the temperature dependence of the soot yield occurs at a temperature of \( \approx 1700–1800 \) K, in contrast to the experimentally observed maximum at \( \approx 2100 \) K. In addition, the measured and predicted values of the soot yield differ significantly. These differences are much smaller for the pyrolysis of ethylene (a hydrocarbon with a double bond) behind shock waves.

Such obvious discrepancies between simulation results and experimental data for the pyrolysis of acetylene suggest that acetylene is the most suitable object for a further refinement of the detailed kinetic model of soot formation. On the one hand, the pyrolysis of acetylene leads to the formation of polyacetylenic hydrocarbons; on the other, it produces, although in significantly smaller amounts, aromatic (from one to two aromatic rings) and polyaromatic (composed of several aromatic rings) hydrocarbons.

Thermal decomposition of acetone can be considered as a source of methyl radicals. Thermal decay of propane is also can be considered as a source of a number of odd-carbon radicals. At the same time, acetylene pyrolysis gives mainly even-carbon fragments and molecules. According to our model of soot formation, the process in acetylene–argon mixtures proceeds largely through a single polyyne-dominated pathway of soot nucleation, while addition of acetone or propane opens an additional aromatic pathway of soot nucleation, thereby increasing the overall soot yield.

Experimental studies and detailed kinetic simulations of the formation of soot particles during pyrolysis of mixtures of acetylene with acetone and propane behind reflected shock waves are the major goals of the current work.

2. Experimental
A stainless steel shock tube, with an inner diameter of 75 mm, driver section length of 1.5 m, and driven section length of 3.2 m, was used.

The low-pressure section was evacuated with two 2-NVR-5D forepumps to a residual pressure of \( 10^{-2} \) Torr and with an NVDS-100 oil diffusion pump to \( 10^{-3} \) Torr. The residual pressure was monitored with a VIT-2 ionization–thermocouple vacuum gage. The high-pressure section was evacuated with a 2-NVR-5D forepump through a liquid-nitrogen trap to a residual pressure of 0.1 Torr. Air leakage into the driven section did not exceed \( 10^{-4} \) Torr/min. Before each experiment, the low-pressure section was purged twice with argon used for preparation of the mixtures, with intermediate pumping to \( 10^{-1} \) Torr.

The parameters of the gas behind the incident and reflected shock waves were calculated from the initial pressure, mixture composition, and incident shock wave velocity using the theory of ideal flow in a shock tube [22]. The velocity of the incident shock wave was measured over two measuring distances with three pressure sensors (\( D_1, D_2, D_3 \)). The \( D_1D_2 \) and \( D_2D_3 \) distances were 528 and 281 mm, respectively. The endmost sensor, \( D_3 \), was positioned 40 mm upstream of the observation section of the shock tube. The pressure transducers, with a sensing element 1 mm in diameter, were made from piezoceramics (lead zirconate titanate). They were coated with a protective wax layer of 0.3–0.5 mm thick. The sensors were mounted flush with the inner wall of the shock tube. The signals generated by the sensing elements of the pressure sensors during the passage of the shock wave were fed, through emitter followers, into G5-15 generator amplifiers and then into Ch3-33 frequency meters operating in the time measurement mode.

The shock wave was generated by a spontaneous burst of one or several aluminum diaphragms of 0.05–0.2 mm thick, depending on what conditions were to be achieved behind the incident or reflected shock wave. The diaphragms were placed in a special-purpose holder between the driver and driven sections, where they were secured with two vacuum rubber rings.

The driver gas was helium. Since the diaphragms ruptured at a nearly the same driver-gas pressure, the temperature behind the incident or reflected shock wave could be additionally
adjusted by diluting helium driver gas with air: the lower the temperature to be achieved behind the shock wave, the higher the percentage of air should be added.

The following gases were used: acetylene (technical grade A, Lentehgaz, Russia), propane, and argon (NII KM Company Limited, Russia). Acetylene was certified to a purity of not less than 99.5%, with the content of air (primary impurity) and other low-soluble gases being within 0.5%. To remove acetone vapor, acetylene was withdrawn from a 40 L bottle into a 10 L gasometer filled with a saturated aqueous solution of sodium chloride. In preparing the test mixtures, acetylene from the gasometer was sequentially passed through a silica gel trap (calcined and cooled in a desiccator) and an empty trap cooled to $-8^\circ$C (using a snow–ice–$\text{CaCl}_2$ ternary mixture).

A gas-chromatography analysis showed the following concentrations of hydrocarbons in $\text{C}_2\text{H}_2$: 0.21 wt % $\text{CH}_4$ and 0.006 wt % $\text{C}_2\text{H}_4$, with no acetone traces found. Further, acetylene was diluted manometrically with argon to 4.8 mol %. The partial pressure of acetylene in the mixture did not exceed 0.5 bar. Acetone was introduced into test mixtures by evaporating analytical grade liquid acetone. The following test mixtures were experimentally investigated: 5.0 mol % $\text{C}_2\text{H}_2 + 95.0$ mol % Ar, 4.0 mol % $\text{C}_2\text{H}_2 + 1.0$ mol % $(\text{CH}_3)_2\text{CO}$ (acetone) + 95.0 mol % Ar, and 4.0 mol % $\text{C}_2\text{H}_2 + 1.0$ mol % $\text{C}_3\text{H}_8 + 95.0$ mol % Ar. The emission and absorption signals from the soot particles were recorded at the same cross-section located at a distance of 15 mm from the endplate of the shock tube. From these measurements, the time profiles of the soot particle temperature and soot particle yields were obtained [14]. To determine the soot yield and the temperature of the soot particles, we used the two-beam absorption–emission method. The light beams of the emission and absorption channels passed through the same cross-section of the shock tube, perpendicular to each other. The measurements were performed at a wavelength of 632.8 nm, isolated with two DMR-4 monochromators, one in each channel. The light signals were converted into electric signals with the help of FEU-39A photomultipliers. The emission channel was calibrated using a 300-W SI-10-300 tungsten band lamp, operating at a current of 22 A, which corresponds to a brightness temperature of 2196 K at $\lambda = 632.8$ nm.

3. Kinetic model

The formation of soot particles was simulated with the use of the kinetic mechanism developed in our earlier study [7]. The kinetic mechanism of gas-phase reactions is based on the USC-Mech II model [23], which describes the oxidation of H$_2$ and CO and the high temperature pyrolysis and oxidation of C$_1$–C$_4$ hydrocarbons. We substantially extended this mechanism so as to allow for soot formation. In particular, we included a number of additional routes of the formation and growth of PAHs (up to coronene) and reactions involving C$_3$, C$_5$, and C$_7$ hydrocarbon fragments. Thus, our kinetic mechanism consists of the following parts: HACA mechanism of the consecutive growth of PAH molecules, phenyl radical–benzene molecule recombination reactions, cyclopentadienyl recombination reactions, and soot nucleation from unsaturated aliphatic hydrocarbons. The principles of constructing this kinetic mechanism were outlined in our earlier works [7, 21, 24].

A new feature of the refined kinetic mechanism is that the main set of gas-phase reactions from paper [25], which was a part of our previous mechanism, was entirely replaced by the set of reactions from [23]. The kinetic model of soot formation was supplemented by the reaction of soot nucleation from diacetylene dimers. The rate constant of the surface growth of soot particles involving acetylene molecules was decreased. This rate constant in the new model is identical to the recommended value for the surface growth of soot particles [25]. The reactions leading to the formation of aromatic components from C$_8$H$_5$ aliphatic hydrocarbons were excluded from the set of gas-phase reactions. The thermodynamic data used in the model have been considerably updated based on the data reported in [23]. For the species not included in the reaction mechanism and thermodynamic data file given in [23], the chemical reactions, rate constants, and thermodynamic data were taken from [26, 27].
According to our soot formation model, soot nuclei are polyaromatic structures formed by the combination of relatively small polyaromatic molecules (with two or three aromatic rings) with their radicals or such radicals with each other. The new version of the mechanism allows for the formation of soot nuclei from $\text{C}_8\text{H}_4$ unsaturated aliphatic hydrocarbons. We cannot state that the formation of a polyaromatic structure takes place in the first step of the interaction between these hydrocarbons. However, the intramolecular conversion of the $\text{C}_8\text{H}_4$–$\text{C}_8\text{H}_4$ complex can well yield a polyaromatic structure similar to the carbon framework of the pyrene molecule ($\text{C}_{16}\text{H}_{10}$). The hydrogen atom deficiency in the resulting aromatic structure $\text{C}_{16}\text{H}_8$ makes it very reactive, a feature favorable for rapid growth of the molecule and for subsequent soot nucleation.

The surface growth of soot nuclei occurs on active sites, which result from the hydrogen atom abstraction in reactions involving reactive species from the gas phase. Thus, the model considers two different types of nuclei, namely, those that do and do not have active sites. Altogether, the kinetic model of soot formation considers three different ensembles of species: active nuclei capable of further growing, inactive nuclei having no active sites, and soot particles.

Soot nuclei are activated reacting with $\text{H}$ and $\text{OH}$ radicals and are deactivated reacting with $\text{H}_2$, $\text{H}_2\text{O}$, and $\text{O}_2$. The activated soot nuclei grow through the addition of $\text{C}_2\text{H}_2$, $\text{C}_4\text{H}_2$, and $\text{C}_6\text{H}_2$ molecules from the gas phase (the concentrations of these species are relatively high in the pyrolysis and oxidation of rich aliphatic and aromatic hydrocarbon mixtures), by reacting with polyaromatic molecules and radicals, and via nucleus–nucleus merge (coagulation). Soot nuclei are oxidized by reacting with $\text{O}$ and $\text{OH}$ radicals and are transformed into soot particles without involving gas-phase species. In turn, soot particles grow through the addition of $\text{C}_2\text{H}_2$, $\text{C}_4\text{H}_2$, $\text{C}_6\text{H}_2$ aliphatic molecules and PAH molecules and radicals. Soot particles participate in coagulation reactions. Soot particles are oxidized by reacting with $\text{O}$ and $\text{OH}$ radicals [18].

In our kinetic model of soot formation, the reactions in which soot nuclei form from gaseous aromatic components are considered as irreversible ones. It is, therefore, essential to select the rate of conversion of soot nuclei into soot particles that would ensure the best fit between the calculated and measured time dependences of the soot yield.

Formation, growth, oxidation, and coagulation of soot nuclei and soot particles were described with the use of the discrete Galerkin method [28]. This method was proposed for solving systems of ordinary differential equations for the direct kinetic problem for heterogeneous polymerization [28]. The method is based on the expansion of the heterogeneous component size distribution function in orthogonal polynomials of a discrete variable, namely, the number of monomer units per heterogeneous particle. The error arising from this expansion can be rigorously estimated using the discrete Galerkin method formalism. The orthogonal polynomials of the discrete variable $n$ are constructed using weight functions determined by the type of chemical process. For example, in the case of free-radical polymerization, the weight function is the Schulz–Flory distribution [28]. This type of weight function is related to the Laguerre polynomials of the discrete variable $n$. If the weight function is known, it is possible to calculate the first moments of the size distribution function and to determine the average particle size. The time variation of the particle size distribution function, which is determined by the chemistry of the corresponding components, leads to a complete system of ordinary differential equations for each expansion coefficient. This approach preserves the discreteness of the elementary changes of the microheterogeneous particle in any reaction involving gas-phase and heterogeneous particles and provides means to describe these changes as ordinary elementary chemical reactions for heterogeneous particles of any size.

The underlying ideas of the discrete Galerkin method and the possibility of solving a large number of differential equations for elementary gas-phase reactions were first implemented in the MACRON code [29].

A significantly revised and augmented version of this program was used in our kinetic calculations for soot formation. Comparing the experimental and simulation results, we assumed
Figure 1. Typical (1) absorption and (2) emission signals as functions of time, which is counted off from the arrival of the reflected shock wave front, and the time profiles of (3) temperature and (4) soot yield calculated from the absorption and emission signals for a mixture containing 5% acetylene in argon under different conditions behind the reflected shock wave: (a) \( T_{50} = 1821 \) K, \([M]_{50} = 2.36 \times 10^{-5} \) mol/cm\(^3\), \( P_{50} = 3.53 \) bar; (b) \( T_{50} = 2049 \) K, \([M]_{50} = 1.93 \times 10^{-5} \) mol/cm\(^3\), \( P_{50} = 3.25 \) bar; and (c) \( T_{50} = 2111 \) K, \([M]_{50} = 2.32 \times 10^{-5} \) mol/cm\(^3\), \( P_{50} = 4.02 \) bar. The wavelength of the probe radiation, \( \lambda = 632.8 \) nm. In diagrams (3) and (4), the lines are the results of processing of measured absorption and emission signal, respectively, whereas triangles and squares represent the calculated values of the soot yield and soot particle temperature.

that the optical properties of soot are the same for all hydrocarbons, described by a constant absorption function \( E(m) \), \( E(m) = 0.37 \) [7, 21].

The kinetic model of gas-phase reactions was supplemented by the reactions of pyrolysis and oxidation of \( n \)-hexane and \( n \)-heptane. Note that the kinetic model of soot formation considered here is based on a gas-phase reaction mechanism describing the pyrolysis and oxidation of the initial hydrocarbons and the formation and growth of PAH molecules, up to coronene, via different reaction routes and molecules of unsaturated aliphatic hydrocarbons. The modified gas-phase reaction mechanism consists of 4782 forward and reverse reactions involving 372 different components, with the rate constants of some important reactions depending on the pressure.

The kinetic model was painstakingly tested against numerous experimental data. For this purpose, we performed series of numerical simulations and compared the results with the available experimental data on the time evolution of the concentration of the major gas-phase products formed in the shock-tube pyrolysis and oxidation of acetylene–argon mixtures [30], the same mixtures with hydrogen additives [30], argon–diluted acetylene mixtures with \( \text{N}_2\text{O} \) (a source of O atoms) [31], diacetylene–argon mixtures [32], and acetylene–argon and \( n \)-heptane–argon mixtures [33]. The results of this comparison were reported in [7], which demonstrated a high predictive possibility of the proposed model.

4. Experimental and simulation results. Discussion
Typical oscillograms of the absorption and emission signals as well as results of their processing in order to obtain time profiles of the soot yield and the temperature of the soot particles are displayed in figures 1 and 2. The values \( T_{50} \), \( P_{50} \) and \([M]_{50} \) designate the temperature, pressure
Figure 2. The same as in figure 1, but for a mixture of argon containing 4% of acetylene and 1% of acetone under different conditions behind the reflected shock wave: (a) $T_{50} = 1987$ K, $[M]_{50} = 2.30 \times 10^{-5}$ mol/cm$^3$, $P_{50} = 3.75$ bar; (b) $T_{50} = 2020$ K, $[M]_{50} = 2.35 \times 10^{-5}$ mol/cm$^3$, $P_{50} = 3.89$ bar; and (c) $T_{50} = 2072$ K, $[M]_{50} = 2.30 \times 10^{-5}$ mol/cm$^3$, $P_{50} = 3.91$ bar.

and density of the test mixture just behind the reflected shock wave. In what follows, we have used $E(m) = 0.37 \pm 0.11$ [7] to determine the soot yield $SY$, which was then compared to the calculation results for the tested hydrocarbons (acetylene, acetylene–acetone, and acetylene–propane mixtures with argon).

The thermal decomposition of the acetone molecule produces two CH$_3$ radicals and relatively inert CO molecule. To determine the possible influence of acetone on soot formation, we have performed a series of experiments in which acetylene–argon mixture was seeded with acetone: 4% of acetylene and 1% of acetone in argon. Typical experimental and simulation results for this mixture are shown in figure 2. The experimental data show that the addition of 1% of acetone to a 4% acetylene–argon mixture causes a noticeable increase in the total soot yield and a very weak shift (by $\approx 50$ °C) of the temperature dependence of the soot yield.

In figure 2, the duration of recording of the absorption and emission signals from the ensemble of soot particles was increased 2.5-fold, up to 5000 µs. After the arrival of the rarefaction wave at the observation section (at $\approx 1500$ µs), a decrease in the soot particle temperature (and hence, in the temperature of the buffer gas) is seen. The emission signal from the soot particles begins to decrease considerably, reflecting drop in the temperature. The absorption signals are much less sensitive to temperature changes in the later stages of the process, since the processes of rapid nucleation and surface growth are generally complete by this time. As can be seen in figure 1, the absorption signal still increases after the arrival of the rarefaction wave at the observation section. Figure 2 demonstrates that absorption signals start to decrease just after the observation time of 2000 µs. That is why we present our results for the reactions time of 2000 µs when the absorption signal is maximal and most close to its quasi-stationary level.

By contrast, in the kinetic calculations, the temperature continues increasing because of the condensation process. Therefore, at long times, the experimentally determined values of the soot yield are always smaller than the calculated values, which are obtained without regard for the temperature and gas density decrease associated with the arrival of the rarefaction wave. The experimental results obtained forced us to perform a significant modification of our previous
Figure 3. Experimentally measured and calculated temperature dependences of the soot yield behind the reflected shock wave for the pyrolysis of two different mixtures: 5% acetylene–95% argon mixture and 4% acetylene–1% acetone–95% argon mixture at $P_{50} = 3.5–4.5$ bar, $E(m) = 0.37$, and $\tau_{\text{rcac}} = 2$ ms. Closed and open symbols represent experimental and computational results, respectively; the lines are nonlinear approximations of the calculated values.

Figure 4. Experimentally measured and calculated temperature dependences of the soot yield behind the reflected shock wave for the pyrolysis of two different mixtures: 5% acetylene–95% argon mixture and 4% acetylene–1% propane–95% argon mixture at $P_{50} = 3.5–4.5$ bar, $E(m) = 0.37$, and $\tau_{\text{rcac}} = 2$ ms. Closed and open symbols represent experimental and computational results, respectively; the lines are nonlinear approximations of the calculated values.

kinetic model of soot formation. In particular, in addition to traditional reaction pathways, involving polyaromatic hydrocarbons and radicals thereof, it was necessary to introduce new channels of soot nucleation from unsaturated aliphatic hydrocarbons and to refine the mechanism of the formation of aromatic compounds from large aliphatic hydrocarbons in the gas phase. Figures 3 and 4 demonstrate the influence of acetone and propane additives to acetylene–argon
mixtures on the temperature dependence of the soot yield. The introduction of methyl radicals into the reaction mixture causes a noticeably increase in the soot yield at the maximum of the temperature dependence of the soot yield.

Figures 5 and 6 demonstrate the relative rates of formation and consumption of benzene (A1) molecules and soot nuclei (CH[N]), respectively, for the pyrolysis of a 5% C₂H₂–Ar mixture and a 4% C₂H₂–1% acetone–Ar at T₅₀ = 1900 K, P₅₀ = 4.0 bar. As can be seen from figure 5, in the case of acetylene pyrolysis benzene molecules are formed mainly by the reactions C₃H₃ + C₃H₃ → A₁ and C₄H₄ + C₂H₂ → A₁. A significant contribution to the formation of C₃H₃ comes from the reaction C₂H₂ + CH₃ → C₃H₃ + H. Acetone additives to acetylene make the contribution of the reaction C₄H₄ + C₂H₂ → A₁ negligibly small, so benzene (A₁) and phenyl radicals (A₁-)...
Figure 6. Relative rates of formation and consumption of soot nuclei (integrated, in %) for the pyrolysis of the mixtures of (a) 5% \( \text{C}_2\text{H}_2 \)-Ar and (b) 4% \( \text{C}_2\text{H}_2 \)-1% acetone–Ar at \( T_{50} = 1900 \) K, \( P_{50} = 4.0 \) bar.

are formed mainly by the reactions of recombination of propargyl radicals: \( \text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \rightarrow \text{A1} \) and \( \text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \rightarrow \text{A1-} + \text{H} \). The concentrations of \( \text{C}_3\text{H}_3 \) radicals and benzene molecules \( \text{A1} \) in the pyrolysis of acetylene alone is approximately two orders of magnitude lower than those in the presence of the acetone additive.

Figure 6 displays even more pronounced difference in the kinetic characteristics of formation of soot nuclei during acetylene pyrolysis with and without acetone additives. According to our soot formation model, for the pyrolysis of the unseeded acetylene–argon mixtures, soot nuclei are formed mainly by the reaction of recombination of two polyyne-like fragments: \( \text{C}_8\text{H}_4 + \text{C}_8\text{H}_4 \rightarrow \text{CH[1]} \). Acetone additive drastically changes this nucleation mechanism. In this case, soot nuclei are mainly formed by several pathways with participation of aromatic hydrocarbons and radicals: \( \text{A2R5 + A2R5-} \rightarrow \text{CH[1]} + \text{H} \); \( \text{A2 + A2-2} \rightarrow \text{CH[1]} + \text{H} \); \( \text{A2 + A2-1} \rightarrow \text{CH[1]} + \text{H} \); \( \text{A1C2H + A1C2H-} \rightarrow \text{CH[1]} + \text{H} \); \( \text{A1C2H + A1C2H*} \rightarrow \text{CH[1]} + \text{H} \), where
CH[1]—soot nuclei; A1—benzene; A1—phenyl radical; A1C₂H—phenylacetylene; A1C₂H—phenylacetylene radicals; A2—napthalene; A2-1—1-naphthyl; A2-2—2-naphthyl; whereas the rest of the nomenclature is similar to that used in [25]. For the pyrolysis of the unseeded acetylene–argon mixture, the concentration of soot nuclei is approximately one order of magnitude lower as compared to that for the acetylene–acetone–argon mixture. Qualitatively similar picture is observed when propane is added to acetylene.

5. Conclusion

Therefore, the shock-tube experiments and detailed kinetic simulations demonstrate that acetone and propane additives to acetylene–argon mixtures substantially promote the process of soot formation as compared with that in the pyrolysis of acetylene–argon mixtures. Detailed kinetic simulations qualitatively and even quantitatively reproduce the results of experiments on soot formation in acetylene pyrolysis behind reflected shock waves and the promoting effect of acetone and propane additives. The indicated additives enhance the soot yield because polyyne-dominated pathway of soot nucleation, characteristic of unseeded acetylene–argon mixtures, is augmented by the aromatic pathway, typical of most hydrocarbons.

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