

SOOT FORMATION IN THE PYROLYSIS OF BENZENE/ACETYLENE AND ACETYLENE/HYDROGEN MIXTURES AT HIGH CARBON CONCENTRATIONS

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The soot formation in the pyrolysis of benzene/acetylene mixtures and acetylene/hydrogen mixtures diluted in argon was measured behind reflected shock waves using a light absorption technique. For this process, the induction period τ , the soot growth rate constant k_f , and the soot yield SY were determined. The experiments were performed in the temperature range between 1560 and 2580 K at pressures of 6 and 60 bar, for different carbon concentrations ($1\text{--}16 \times 10^{-6}$ mol/cm³) and different ratios of the components.

For the benzene/acetylene mixtures, the induction times did not show a significant effect related to pressure or mixture ratio and were placed between the induction times for the pure substances. Increasing the benzene/acetylene ratio considerably increases the soot growth rate constant k_f at high temperatures. The previously observed bell shape of the soot yield curves as a function of temperature could be confirmed for all mixtures, with maximum soot yields at a temperature of about 1800 K. The soot yield data obtained for benzene/acetylene mixtures show a remarkable synergistic effect. Increasing the pressure or the benzene/acetylene ratio in benzene-rich mixtures decreases the soot yield. In the case of acetylene/hydrogen mixtures, a considerable suppressive influence of the hydrogen additive on the soot yield was observed.

Soot particle diameters were determined by transmission electron microscopy and can be described by a narrow, log-normal size distribution function. The average particle diameters are in the range of 20 ± 5 nm for all conditions of temperature and pressure employed in this study and they show a tendency to increase with increasing carbon concentration. Assuming spherical particles, final particle number densities in the range of $10^{11}\text{--}10^{13}/\text{cm}^3$ were obtained.

Introduction

The process of soot formation has been investigated for quite some time [1–4]. There are, however, some phenomenological aspects that still need further consideration. Here, results obtained from shock tube pyrolysis experiments are of particular interest. For many hydrocarbons except benzene, the rate of soot formation passes through a maximum around 2000 K [5,6]. In order to obtain further information about the soot formation kinetics in pyrolysis processes at higher temperatures, experiments in binary mixtures have been performed.

There are several papers on soot formation in binary mixtures [7–12]. It was found in shock tube experiments that the addition of acetylene to 1,3-butadiene and to allene increases both the soot yield and the amount of soot [12]. When acetylene is added to benzene, the opposite effects were found. The amount of soot formed increased but the soot

yield decreased. These experiments were performed at pressures between 1 and 3 bar. In Ref. 10 it was concluded that in a flow reactor at near atmospheric pressure and a temperature of 1473 K during pyrolysis of benzene/acetylene mixtures, the soot particle nuclei were formed only from acetylene. A nucleation of soot particles from benzene is assumed to be completely inhibited and its molecules are consumed only by the growth of particles formed from acetylene.

It was shown recently that many features of the soot formation processes change considerably toward higher pressures, especially for pressures above 10 bar [6,13,14]. In order to cover a large range of conditions, the work reported here was devoted to soot formation in shock tube pyrolysis of benzene/acetylene and acetylene/hydrogen mixtures behind reflected shock waves. Experiments were conducted in the temperature interval between 1560 and 2580 K, and for two different pressures, namely, 6 and 60

TABLE 1
Experimental conditions

Series	T (K)	P (MPa)	$C_6H_6:C_2H_2$	$[C]$ (mol/cm ³ /10 ⁶)
1	1670–2150	6.2	1:3	1.2
2	1670–2210	6.2	1:3	5
3	1860–1980	6.1	1:2.5	8.4
4	1560–2580	6.3	1:1	5
5	1850	6.1	1:1	16
6	1650–2250	5.8	2.5:1	12
7	1680–2500	6.0	10:1	9
8	1700–2400	0.64	1:2.5	6
9	1570–2400	0.64	1:1	5
10	1460–2170	0.66	2.5:1	9
11	1600–2400	0.5–11	1:0	0.4–4
12	1600–2400	2.5–5.5	0:1	1–4
Series	T (K)	P (MPa)	$C_2H_2:H_2$	$[C]$ (mol/cm ³ /10 ⁶)
13	1630–2360	6.0	1:1	2
14	1680–2420	6.0	1:1	4

bar. Carbon concentrations were varied from 1 to 16×10^{-6} mol/cm³. The main goal of this investigation was to obtain data about mutual influence of the mixture ratios in benzene/acetylene and acetylene/hydrogen mixtures at high carbon concentrations, and various pressures and temperatures. Investigated were the induction time of soot formation τ , the formal soot growth rate constant k_f , the soot yield SY , and the final particle diameter d .

Experimental

The experimental set-up has been described elsewhere [6,15], therefore, only the main details are given. The experiments were conducted behind reflected shock waves in a 70 mm i.d. steel shock tube with a 4.5 m-long driven section, a 3.5 m-long driver section, and a 28 mm-thick tube wall. Shock speed and the pressure time profile were measured with Kistler piezo-electric pressure transducers. Shock parameters were computed following the standard procedure [16,17] using the measured incident shock speed. The difference between the calculated and the measured pressure was less than 2%, and the estimated accuracy of the temperature calculation is ± 30 K.

The conversion of hydrocarbon to soot was measured via the attenuation of the light beam from a 15 mW He-Ne laser operated at $\lambda = 632.8$ nm, and a 50 mW In-Ga-As laser operated at $\lambda = 1064$ nm. The optical observation plane was positioned 28 mm from the end-plate of the shock tube. The light extinction profiles $I(t)$ were converted into soot yield profiles $SY(t)$ using Beer's law (see, e.g., Ref. 18), a refractive index of $m = 1.57 - 0.56i$, a soot density of 1.86 g/cm³, and the molar mass of carbon M_C .

The test gas mixtures were prepared manometrically and mixed by convection in stainless steel cylinders at least 48 h before use. The gases acetylene ($> 99.6\%$ Linde), hydrogen ($> 99.9\%$ Messer-Griesheim), and argon ($> 99.998\%$ Messer-Griesheim) were used without further purification. Benzene ($> 99.9\%$ Riedel-De Haën) was purified by distillation.

Soot particles were collected on carbon-film-coated copper grids (mesh size 400) and their diameters were determined by transmission electron microscopy (TEM). For several experiments, especially with a high soot volume fraction, the soot formed was collected to determine the specific soot surface area and the final soot yield by the gravimetric method.

Experimental Results

Fourteen series of experiments with various carbon concentrations, acetylene/hydrogen ratios, benzene/acetylene ratios, and two different pressures were performed. The conditions of the experiments are summarized in Table 1.

Time History of Soot Formation

In Fig. 1, one can see time histories of soot formation for a (1:3) benzene/acetylene mixture at 60 bar and a constant carbon concentration of 1.2×10^{-6} mol/cm³. The soot yield profiles were obtained by extinction measurements at a wavelength of 1064 nm. All profiles have a typical induction period and S-shape form. The induction period decreases with temperature. The temperature dependence of the maximum slope of the profiles and

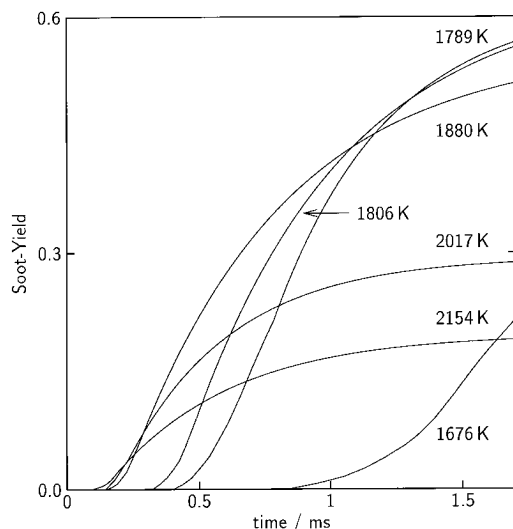


FIG. 1. Six time histories of soot formation measured at a pressure of 60 bar for a (3:1) benzene/acetylene mixture, $[C] = 1.2 \times 10^{-6}$ mol/cm³ and for $\lambda = 1064$ nm. The related temperature is indicated at each curve.

the final soot yields pass through a maximum. In comparison to extinction measurements performed at 633 nm, the induction periods measured were always longer, but the maximum slopes and soot yields after the inflection point did not change with the wavelength.

Induction Time

In the present work, the induction time is defined using the intersection of the tangent at the inflection point of the soot yield curve with the time axis [6,19]. The value of the induction time depends, as mentioned, somewhat on the experimental technique used. However, the order of magnitude and the dependence on parameters such as pressure, temperature, and carbon concentration are similar for different experimental techniques. To fit the induction times, the following expression is used:

$$\tau = A_{\text{Ind}} \cdot \exp(E_{\text{Ind}}/RT)/[C]^n \quad (1)$$

Figure 2 shows the normalized induction times for benzene, acetylene, and their mixtures at 60 bar in an Arrhenius plot. According to Fig. 2, the following parameters are obtained for all mixtures at $\lambda = 633$ nm: $A_{\text{Ind}}^{633} = 4.36 \times 10^{-15}$ sec (mol/cm³)^{0.75}, $E_{\text{Ind}} = 228$ kJ/mol, and $n = 0.75$. The activation energy for the mixtures coincides with that for pure benzene and acetylene [19]. The logarithm of the preexponential factors $\lg(A_{\text{Ind}}^{633})$ are in the middle between those for the pure hydrocarbons. Induction times of

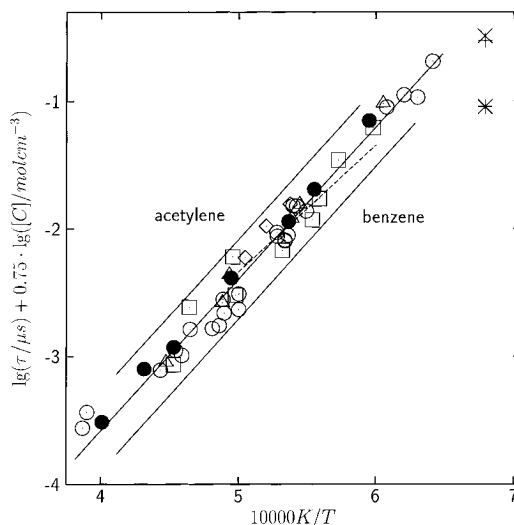


FIG. 2. Arrhenius type plot of the normalized induction time ($\tau \cdot [C]^{0.75}$) for mixtures with various benzene/acetylene ratios (B:A) and carbon concentrations for 60 bar; \square , (B:A) = (1:3), $[C] = 1.2-5 \times 10^{-6}$ mol/cm³; \diamond , (B:A) = (1:2.5), $[C] = 8.4 \times 10^{-6}$ mol/cm³; \odot , (B:A) = (1:1), $[C] = 5-16 \times 10^{-6}$ mol/cm³; \triangle , (B:A) = (2.5:1), $[C] = 12 \times 10^{-6}$ mol/cm³; \bullet , (B:A) = (10:1), $[C] = 9 \times 10^{-6}$ mol/cm³; solid lines, best fits for acetylene (upper), benzene/acetylene (middle) and benzene (lower); $+$, benzene, $[C] = 3.9 \times 10^{-6}$ mol/cm³ [10]; \times , acetylene, $[C] = 1.3 \times 10^{-6}$ mol/cm³ [10]; \circ , benzene/acetylene, $[C] = 5.2 \times 10^{-6}$ mol/cm³ [10]; dashed line, acetylene, $[C] = 2 \times 10^{-6}$ mol/cm³ [24].

the mixtures at 6 bar are close to that for pure acetylene, and therefore, these data are not indicated separately in Fig. 2. Using different wavelengths, the induction time is usually longer in the case of the longer wavelength. For $\lambda = 1064$ nm, we obtained a slightly higher preexponential factor ($A_{\text{Ind}}^{1064}/A_{\text{Ind}}^{633} \approx 1.3$) and practically the same apparent activation energy.

For a (1:1) acetylene/hydrogen mixture at 60 bar and a carbon concentration of 4×10^{-6} mol/cm³, the induction times coincide with those of ethylene [6], containing the same carbon and hydrogen concentration, and are 25% longer than for pure acetylene.

Soot Growth Rate

The soot volume fraction profiles after the inflection point are approximated by an empirically obtained first order rate law, where k_f is the soot growth rate and f_v is the soot volume fraction

$$\frac{df_v}{dt} = k_f \cdot (f_{v\infty} - f_v) \quad (2)$$

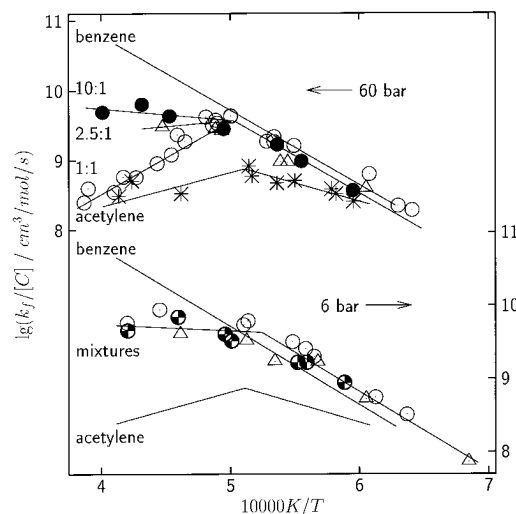


FIG. 3. Temperature dependence of the normalized first order rate constant ($k_f/[C]$) for benzene, acetylene, benzene/acetylene, and acetylene/hydrogen mixtures at 6 bar (lower part) and 60 bar (upper part). For 60 bar: \circ , (B:A) = (1:1), $[C] = 5 \times 10^{-6}$ mol/cm³; Δ , (B:A) = (2.5:1), $[C] = 12 \times 10^{-6}$ mol/cm³; \bullet , (B:A) = (10:1), $[C] = 9 \times 10^{-6}$ mol/cm³; \circ , (C₂H₂:H₂) = (1:1), $[C] = 2-4 \times 10^{-6}$ mol/cm³; solid lines, best fits, benzene (upper), acetylene and acetylene/hydrogen (lower) [22]. For 6 bar: \bullet , (B:A) = (1:2.5), $[C] = 6 \times 10^{-6}$ mol/cm³; \circ , (B:A) = (1:1), $[C] = 5 \times 10^{-6}$ mol/cm³; Δ , (B:A) = (2.5:1), $[C] = 9 \times 10^{-6}$ mol/cm³; solid lines, best fits, benzene (upper) and acetylene (lower).

$$SY_{\infty} = \frac{f_{v\infty}}{[C]_{\text{total}}} \cdot \frac{\rho_{\text{soot}}}{M_C} \quad (3)$$

Equations 2 and 3 give a convenient way to calculate k_f and the final soot yield SY_{∞} . For near atmospheric pressure flames, k_f has been interpreted as an effective measure of the “active lifetime” of soot particles, assuming that they are losing their reactivity [5,13,14,20,21].

Figure 3 shows the temperature dependence of the normalized rate constant ($k_f/[C]$) for several benzene/acetylene mixtures at 6 and 60 bar, acetylene/hydrogen mixtures at 60 bar, and for different carbon concentrations in an Arrhenius diagram. In the upper part of Fig. 3, rate constants at 60 bar for three benzene/acetylene mixtures, namely, (B:A) = (1:1), (2.5:1), (10:1), two (1:1) acetylene/hydrogen mixtures, pure acetylene, and pure benzene are shown. Carbon concentrations are given in Table 1 (series 4, 6, 7, 11–14). For temperatures below 1950 K, all curves, except those for the pure acetylene and acetylene/hydrogen mixture, have an apparent activation energy of 205 kJ/mol and a preexponential factor of about 1.2×10^{15} cm³/mol/s. The soot

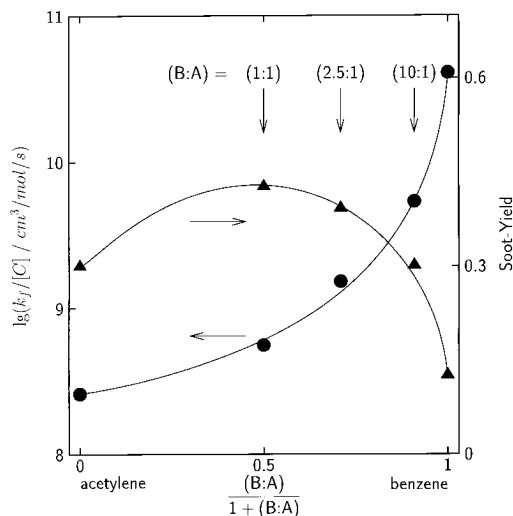


FIG. 4. The benzene mixture fraction dependence of the normalized first order rate constant ($k_f/[C]$) (\bullet) and the final soot yield (SY_{∞}) (\blacktriangle) for benzene, acetylene, and their mixtures at 60 bar and 2400 K. The related mixture composition is indicated at each point.

growth rate constants in the pyrolysis of acetylene and acetylene/hydrogen mixtures coincide [22], and their apparent activation energy is lower than for other hydrocarbons within the temperature range used.

While decreasing the benzene/acetylene ratio, the apparent activation energy on the high-temperature side decreases toward a negative value. This effect is shown more explicitly in Fig. 4 at 2400 K. Here, the normalized rate constants are given for five benzene mixture fractions (B:A)/[(B:A) + 1]. Increasing the benzene mixture fraction from zero to one increases the rate constant more than two orders of magnitude. A small addition of acetylene to benzene leads to a strong decrease of k_f .

In the lower part of Fig. 3, rate constants determined at 6 bar for five benzene/acetylene mixtures, namely (B:A) = (1:2.5), (1:1), (2.5:1), pure acetylene, and pure benzene (series 8, 9, 10, 11, and 12) are shown. Again, the apparent rate constant for temperatures below 1950 K is similar to that for benzene, and for higher temperatures it depends on the fuel composition. All rate constants for the mixtures seem to be slightly higher than for 60 bar. The differences in k_f for the mixtures investigated are smaller than the scattering of the data.

Soot Yield

The final soot yield is defined as carbon finally present as soot referred to the total carbon content of the mixture. The soot yield curves show the bell

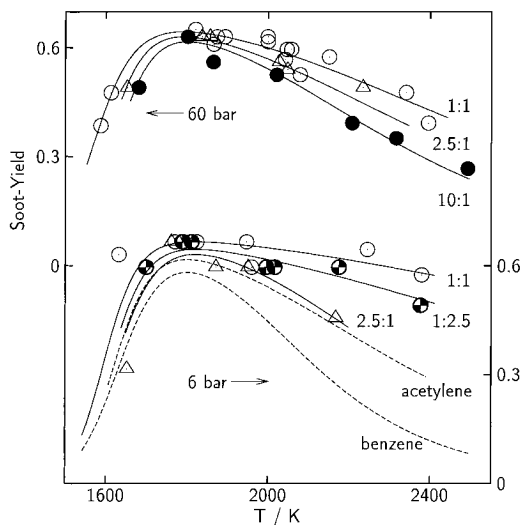


FIG. 5. Temperature dependence of the soot yield in the pyrolysis of benzene, acetylene, and their mixtures at pressures of 6 bar (lower part) and 60 bar (upper part). For 60 bar: \circ , (B:A) = (1:1), $[C] = 5 \times 10^{-6}$ mol/cm³; \triangle , (B:A) = (2.5:1), $[C] = 12 \times 10^{-6}$ mol/cm³; \bullet , (B:A) = (10:1), $[C] = 9 \times 10^{-6}$ mol/cm³; for 6 bar: \oplus , (B:A) = (1:2.5), $[C] = 6 \times 10^{-6}$ mol/cm³; \circ , (B:A) = (1:1), $[C] = 5 \times 10^{-6}$ mol/cm³; \triangle , (B:A) = (2.5:1), $[C] = 9 \times 10^{-6}$ mol/cm³; dashed lines, best fits for acetylene and benzene, $[C] = 4 \times 10^{-6}$ mol/cm³ [19].

shape observed in previous papers for near atmospheric pressure [18,23] and for higher pressures [15]. Soot yields for benzene/acetylene mixtures from the same sets of experiments that were used to describe k_f are shown in Fig. 5 for pressures of 6 and 60 bar. All soot yield curves shown there exhibit a pronounced maximum at about 1800 K (see also Fig. 1). For comparison, data for pure acetylene and pure benzene [19] are included ($[C] = 4 \times 10^{-6}$ mol/cm³). The soot yields for the (1:1) mixture are higher than for the pure hydrocarbons. For a temperature of $T = 2400$ K, the soot yield increases two to four times compared with that for benzene. The highest soot yields determined here are related to the smallest investigated benzene/acetylene ratio (1:1) and the lowest carbon concentration (5×10^{-6} mol/cm³). This effect is shown more explicitly in Fig. 4 for five benzene mixture fractions (B:A)/(B:A + 1). Practically all soot yields at high temperature are higher than for the pure compounds at equal carbon concentration.

Figure 6 presents the results for the soot yield from two (1:1) acetylene/hydrogen mixtures with different carbon concentrations of 2 and 4×10^{-6} mol/cm³, respectively. Soot yield data for ethylene (with the same C:H ratio as the mixtures) and for acetylene are shown for comparison ($[C] = 4 \times 10^{-6}$

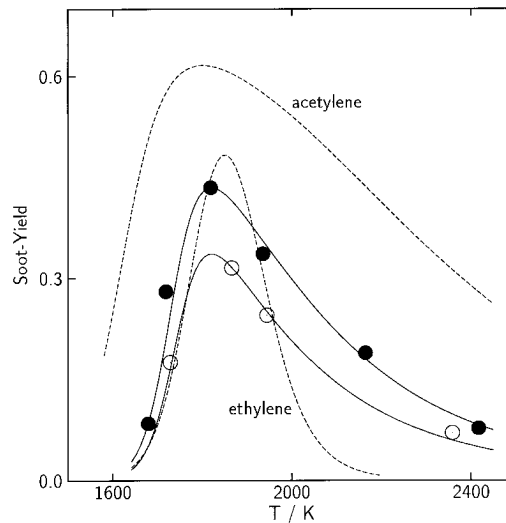


FIG. 6. Temperature dependence of the soot yield in the pyrolysis of acetylene/hydrogen mixtures at a pressure of 60 bar for two different carbon concentrations and an acetylene/hydrogen ratio equal unity. \bullet , $[C] = 4 \times 10^{-6}$ mol/cm³; \circ , $[C] = 2 \times 10^{-6}$ mol/cm³; solid lines, best fits; dashed lines, best fits for ethylene (lower) and for acetylene (upper), $[C] = 4 \times 10^{-6}$ mol/cm³ [19].

mol/cm³) [19]. Again, the soot yield maxima are near 1800 K. The addition of hydrogen reduces the soot yield from acetylene approximately to the data for ethylene with the same C and H atom concentration. The slope of the soot yield curve for the acetylene/hydrogen mixture is, however, distinctly different from that for ethylene, showing much higher soot yields at high temperatures. A reduction of the carbon concentration for the acetylene/hydrogen mixture by a factor of 2 reduces the soot yield by a factor of approximately 0.7.

Particle Size

Soot particles were deposited on grids under all conditions given in Table 1. The samples were examined by means of TEM. The visual impression of all micrographs obtained from different experiments is very similar. The micrographs show spherical primary particles which are mainly agglomerated in long chains. The diameters of the primary spherical particles can be described by a log-normal size distribution function with a geometric standard deviation of $\sigma_g = 0.15 \pm 0.05$. The average soot particle diameters are in the range of 15–25 nm for all experimental conditions employed and they show a tendency to increase with increasing carbon concentration. Furthermore, the specific surface was determined by the method of nitrogen adsorption at the temperature of liquid nitrogen. Therefore, 20–200

mg soot (depending on the final amount of soot) was sampled mechanically, corresponding to 90% of the optically determined soot yield. A specific surface of $120 \text{ m}^2/\text{g} \pm 10\%$ was found, independent of the experimental conditions employed. This holds for a typical final soot volume fraction of 5×10^{-5} in a final soot particle surface of 110 cm^2 in 1 cm^3 gas volume. The specific surfaces obtained may be influenced by the physical and chemical properties of the soot particle surface and may not depend only on the geometric surface of the particles.

Discussion

Soot formation experiments in the pyrolysis of benzene/acetylene and acetylene/hydrogen mixtures behind reflected shock waves were performed in order to check the influence of the ratio of the mixture components on the soot formation process.

The induction times in the benzene/acetylene pyrolysis are between those for the pure hydrocarbons at 60 bar. It should be noted, however, that a small carbon fraction coming from acetylene leads to a strong increase of the induction period. In the case of 3.3% "acetylene-carbon" of the total carbon concentration, two times longer induction times than for pure benzene under otherwise equal conditions were measured (see the filled circles in Fig. 2). Therefore, an acetylene addition to benzene definitely increases the delay for the start of the soot formation.

In the work of Tesner et al. [10], induction times at 1473 K were measured in a flow reactor with high concentrations of pure benzene, acetylene, and a (1:1) benzene/acetylene mixture. The normalized induction times for both pure fuels were placed on the extrapolated benzene fit in Fig. 2. The normalized induction time for their mixture is three times shorter. This is different from the results reported here and may be due to the different technique applied. Induction times were obtained from Fussey et al. [24] using the shock tube technique for 2% acetylene in argon at 10 bar ($[C] = 2 \times 10^{-6} \text{ mol/cm}^3$). Normalizing this data using equation 1 shows that their data are in the same range as our data but with a somewhat lower apparent energy of activation.

The preexponential factor of k_f depends somewhat on the fuel structure and pressure. Decreasing the pressure from 60 to 6 bar increases the preexponential factor for the mixtures slightly. The temperature dependence of the formal rate constant k_f is similar for several hydrocarbons at temperatures below 1950 K. Toward higher temperatures, k_f for many hydrocarbons passes through a maximum at a temperature of $(1950 \pm 50) \text{ K}$ and decreases with further increasing temperature [5,6,19]. One exception is benzene, where the k_f grows continuously toward

higher temperatures [6,19]. The benzene/acetylene mixtures studied show the same temperature dependence on k_f as aliphatic and aromatic hydrocarbons below the maximum temperature at 60 bar. For higher temperatures and with increasing acetylene content in the mixture, the slope of the k_f curve changes from that for pure benzene toward zero, and finally to negative values, as for acetylene. The rate constants of the (1:1) benzene/acetylene mixture are similar to those of aromatic hydrocarbons with one short side chain such as phenylacetylene, toluene, and styrene at 60 bar [19,22]. This effect is clearly demonstrated for 2400 K in Fig. 4 and has to be seen in connection with the induction periods and especially with the soot yields.

Below 1800 K, the influence of the mixing ratio on the soot yield is relatively small. Above 2000 K, the influence of the mixture composition becomes quite strong, and high soot yields are reached (see Figs. 4 and 5). In fact, the soot yields for all benzene/acetylene mixtures investigated in that temperature range are higher than those for the pure fuels. Obviously, a marked synergistic effect takes place for benzene/acetylene mixtures. Frenklach et al. [12] performed shock tube pyrolysis experiments at 2–3 bar and carbon concentrations between 0.5 and $1 \times 10^{-6} \text{ mol/cm}^3$. They reported that addition of allene and 1,3-butadiene to acetylene increases soot yields. Decreasing soot yields were found for benzene/acetylene mixtures. This differs from the results reported here for high carbon concentrations and pressures.

For the acetylene/hydrogen mixtures investigated, a strong soot suppression effect was observed. Induction times are longer and soot yields are lower than for pure acetylene. Decreasing the carbon concentration by a factor of two in the mixture decreases the soot yield less than a factor 2. This is similar to the behavior of pure acetylene [19]. Soot yield reduction by the addition of hydrogen to acetylene was also reported in Ref. 12 at the conditions mentioned above. Their soot yield maximum at a temperature of 2150 K was reduced from 3% to 1%. No soot was found at 1800 K, where the soot yield maximum appears for the conditions applied here. That difference is probably due to the different experimental conditions and especially the different carbon concentrations used. High carbon concentrations broaden the soot yield curves toward higher temperatures, shown in Fig. 6. These experiments with acetylene/hydrogen mixtures show clearly that the beginning of the pyrolysis process has a pronounced influence on the formation of soot precursors.

The particle number densities have not been measured by optical methods in these experiments. From the TEM pictures and the known soot yields, one may, however, estimate the number density of soot particles. For an experiment at 60 bar and a carbon concentration of 10^{-5} mol/cm^3 , a final soot volume fraction of $f_{\text{soot}} \approx 5 \times 10^{-5}$ was found. The

average final particle diameter was determined by TEM to be 20 nm. This leads to a mean particle volume of $\bar{v}_\infty = 4 \times 10^{-18} \text{ cm}^3$. The number density is described by $N = f_\infty/\bar{v}$. This results in a final number density of approximately $10^{13}/\text{cm}^3$. For the other experiments, similar results can be calculated. These high particle number densities indicate that the coagulation must come to an end quite early in the soot formation process. From the Smoluchowski equation for coagulation

$$\frac{dN}{dt} = -k_{\text{coag}} \cdot N^2 \quad (4)$$

one can estimate a characteristic half time of coagulation $\tau_{\text{coag}} = (k_{\text{coag}} \cdot N)^{-1}$. For the shocked gas, a Knudsen number in the order of 1 was calculated. This value is usually ascribed to the so-called transition regime from the slip flow to continuum regime [25]. For an approximate calculation, this value can be used in the case of the free-molecular regime [26]. A calculation on the basis of the theoretical expression gives characteristic times for coagulation under the conditions applied in the range of 10–100 μs . Therefore, especially for high temperatures, the coagulation of particles must play its essential role at the beginning of the soot formation process. The particles loose their ability to stick together very early, otherwise N_∞ would be much lower.

The formation of high soot yields in the mixtures of benzene/acetylene at high temperatures comes together with a drop of the formal rate constant k_f , which is a measure for the active life time ($\tau_f = k_f^{-1}$) for soot formation. Its value may be influenced by properties of the particles as well as by properties of the reacting gas mixture. This decrease of τ_f could explain the right part of the soot yield curve in Fig. 4. Apparently, it does not hold for acetylene itself. That might be taken as a hint for the influence of the gas-phase composition during soot formation. After long times, the gas-phase composition will be nearly the same for both pure fuels in Fig. 4. A quantitative description of the effects reported here requires fairly detailed information, especially about the behavior of the particles, and is too lengthy to be given here.

For rich, premixed ethylene/air flames burning at 70 bar and a surplus carbon concentration of $[C]_{\text{surplus}} = 10^{-5} \text{ mol}/\text{cm}^3$, a particle diameter of 20 nm, a number density of $10^{13}/\text{cm}^3$, and a final soot particle surface of $100 \text{ cm}^2/\text{cm}^3$ were found [27,28]. These three important parameters for the soot formation process coincide with our pyrolysis data. This indicates that the different chemical environment in high-pressure flames, especially the oxygen-containing species, seem to have little influence on the later part of the soot formation process.

Conclusion

The shock tube pyrolysis experiments with benzene/acetylene and acetylene/hydrogen mixtures at high carbon concentrations ($1\text{--}16 \times 10^{-6} \text{ mol}/\text{cm}^3$) and pressures showed the following:

- Mean TEM particle diameters are obtained in the range of 20 nm. They can be described by a narrow log-normal size distribution function. The average specific surface of the soot particles is $120 \text{ m}^2/\text{g}$. At the high carbon concentrations applied, the particle coagulation stops early, and high final particle number densities could be calculated.
- In the case of benzene/acetylene mixtures, the induction times are placed between those for pure benzene and acetylene.
- For temperatures below 1800 K, the soot growth rate constants are nearly the same for the pure fuels and the mixtures applied. For temperatures above 2000 K, the soot growth rate constant for the mixtures drop from the values for pure benzene to pure acetylene (at 2400 K for two orders of magnitude).
- For temperatures higher than 2000 K, soot yields are definitely higher for the (1:1) benzene/acetylene mixture than for the pure fuels.
- In the case of acetylene/hydrogen mixtures, a considerable suppression influence of hydrogen regarding induction time and soot yield was found.

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COMMENTS

Pavel A. Tesner, VNIIGAS, Russia. What is your opinion about your experimental result that the induction time for acetylene-benzene mixture falls between that of acetylene and benzene?

Author's Reply. The behavior of the induction periods for the benzene/acetylene mixtures compare well with the behavior of benzene or acetylene with other hydrocarbons like n-hexane, ethylene etc.

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R. D. Kern, University of New Orleans, USA. Shock tube experiments on benzene pyrolysis show considerable decomposition at 2400 K [1]. The products of the decomposition are mostly C_2H_2 , C_4H_2 and H_2 . The decomposition of benzene is strongly endothermic (≈ 136 kcal/mol), while the formation of soot particles is exothermic. What are the magnitudes of the temperature fluctuations in the reflected shock zone for the benzene mixture due to decomposition and soot formation at 2400 K? Is comparison of the soot yields of pure benzene and pure acetylene at

the reaction temperature of 2400 K valid? Your result is that the soot yields of C_6H_6 and C_2H_2 are approximately equal at 2400 K. However, pure C_6H_6 at 2400 K is mostly a mixture of its products. Is this the reason that the soot yields of C_6H_6 and C_2H_2 are approximately the same value at 2400 K?

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Author's Reply. The reaction enthalpies of the benzene and acetylene pyrolysis do indeed influence the temperature behind the shock wave. This was one of the reasons, why we performed the experiments at high carrier gas densities. Under the conditions in the paper the temperature variation due to the pyrolysis reaction was, based on the analysis of the products in the pyrolysed gases, generally below 50 K. The soot yields at 2400 K are given in the paper (for acetylene about 30% and for benzene about 13%). The remaining carbon is mostly present as acetylene.