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On the Mechanism of Soot Particle Formation

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Abstract—The results of experiments on the isothermic pyrolysis of acetylene, benzene, and diacetylene in a flow reactor near a low-temperature threshold of soot formation are presented. Diacetylene showed a much higher ability to form soot, coke, and tar than the other hydrocarbons. The threshold temperature of soot formation from diacetylene (800 K) was found to be lower than the threshold temperatures for benzene (1230 K) and acetylene (1200 K) for the same pyrolysis time (0.17 s) and equal hydrocarbon concentrations (on the basis of C atoms). The induction periods of soot formation for acetylene and benzene at 1100–1200 K, which were estimated from experiments, correlated well with literature data extrapolated from the high-temperature region. Invisible soot particles (0.3–0.5 μm) and particles at different steps of carbonization were found among the products of low-temperature pyrolysis. Experimental data were analyzed and compared within the framework of two soot formation theories presented in the literature (the "acetylene" and "aromatic" theories). The contribution of the process of polyyne polymerization in a gas phase to the formation of a soot aerosol is discussed.

INTRODUCTION

By now, two main hypotheses explaining the mechanism of soot formation in the combustion and thermal decomposition of hydrocarbons are available in the literature (Fig. 1). The first hypothesis goes back to Berthelot and suggests that the formation of soot particles follows the "acetylene route" [1, 2]. The supporters of this hypothesis emphasize that the thermodynamic stability of acetylene (as well as higher polyynes $C_{2n}H_2$, $n = 2, 3, \ldots$) increases with increasing temperature, whereas the stability of all other types of hydrocarbons decreases (Fig. 2). The reason for this phenomenon was found recently. The experimental and theoretical studies [3, 4] showed that the most stable structures of carbon clusters (up to C_{20}) are chains and rings (analogs of infinitely long chains). Thus, at a high temperature, when C–H bonds become relatively weak, the carbon skeletons of acetylene and polyynes are retained as the most stable structures among all possible structures of small carbon clusters. This allows us to suggest that this acetylene route may be the closest approximation to the mechanism of soot aerosol formation at high temperatures, which takes place during the condensation of pure carbon vapor [5]. An increase in the thermodynamic stability of acetylene with increasing temperature is the reason for the practically complete decomposition of all hydrocarbons into acetylene in flames. Concentration of acetylene dominates in the soot zone of a flame [6–8]. Recently, a kinetic model of soot formation was suggested. This model, which is a development of the acetylene route, considers the formation of a primary soot aerosol as the chemical condensation (polymerization) of "supersaturated polyyne vapor" [9–12]. This model makes it possible to calculate the main parameters of the pyrolysis process, such as the induction period of soot formation, the yield of soot particles, the yield of soot, and the effective rate constant of soot particle growth. These calculations are in agreement with the experimental data for various hydrocarbons including methane, ethylene, acetylene, and benzene. Recently, this approach was successfully used by other investigators [13].

In contrast to the acetylene route, the authors of the "aromatic" hypothesis of soot formation (Fig. 1) consider primary soot particles to be formed as a result of the coagulation of bulky polycyclic aromatic molecules [7, 14–16]. The intensive development of this hypothesis began in the 1970s simultaneously with the wide application of mass spectrometry, electron microscopy, and gas chromatography in experimental studies on the mechanism of soot formation. At that time, spherical particles 1.5 nm in diameter (2000 amu) were detected and characterized by electron microscopy and mass spectrometry in a premixed low-pressure flame of C_2H_2/O_2. The concentration of these particles has a maximum just before the appearance of a soot aerosol [17,18]. These particles were presumed to be soot nuclei, and their formation was explained by coagulation of high-molecular-weight components of the gas phase. Molecules with a mass of up to 300 amu were identified in the soot zone of a flame by gas chromatography and mass spectrometry [6–8, 19, 20]. Among them, the highest concentrations were found for lower polyynes (C_4H_2, C_6H_2, and C_8H_2) and polycyclic aromatic hydrocarbons (PAH) from naphthalene to coronene. Concentrations of all these hydrocarbons exhibited a maximum just before the appearance of soot particles. The further works showed that the aromatic structures from naphthalene to coronene constitute only a limited portion of the matter that can be collected and condensed in the soot zone of enriched flames. The residue is a tar-like yellowish brown material consisting

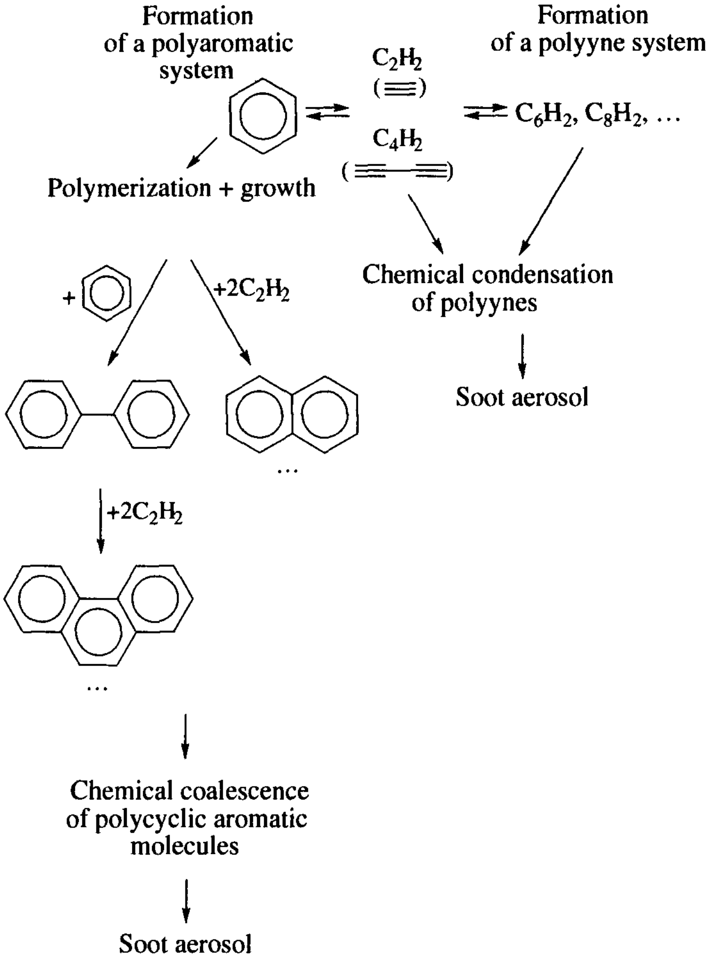

Fig. 1. "Acetylene" and "aromatic" hypotheses of soot aerosol formation.

of substances with masses in the range of 300–3000 amu. These substances cannot be analyzed by gas chromatography or identified by chemical analysis [19–22]. They were found to have concentrations much higher than the concentrations of PAH and comparable with the concentration of soot material [23].

Theoretical development of the aromatic route of soot formation consisted in the construction of a kinetic mechanism of the formation of PAH molecules in soot flames and in the pyrolysis of hydrocarbons and in the demonstration of the way in which aromatic components coagulate to form primary aerosol particles. Various kinetic mechanisms of the growth of polycyclic aromatic molecules in a gas phase were suggested (Fig. 3). This growth proceeds either as the consecutive buildup of cycles in reactions with the participation of acetylene (the H abstraction–C_2H_2 addition mechanism suggested in [7, 14]) or by the polymerization mechanism, which was considered in detail in [24] using pyrene as an example. The estimates [25] show that van der Waals interactions between polycyclic aromatic molecules with molecular weights of 600 amu or higher become comparable with chemical interactions (about 22 kcal/mol). As a result, the collision complex of these molecules is long-lived. In addition, a high concentration of radicals in the soot zone of a flame results in the fact that a considerable portion of PAH particles of this size can have one or several free valances [26]. Therefore, the probability of chemical

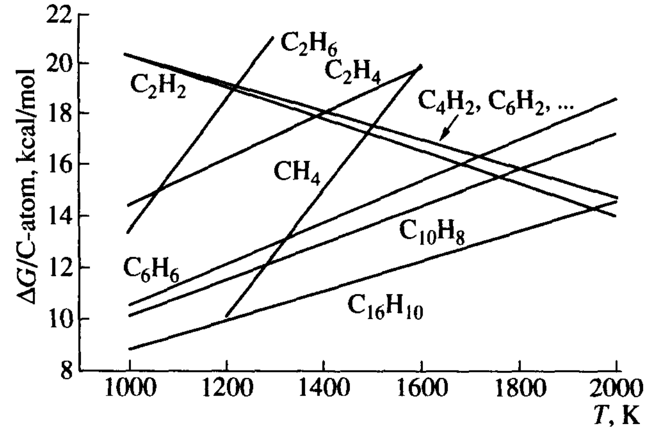

Fig. 2. Changes in the Gibbs free energy in the reactions mC(graphite) + $n/2H_2 = C_mH_n$.

bonding of large PAH molecules at a collision (coalescence efficiency) was suggested to be close to unity. In recent years, many efforts have been made to develop a quantitative model of a soot flame. This model is based on a hypothesis of the growth of polycyclic aromatic molecules and their coagulation [14, 27, 28]. Unfortunately, this model was never used for systematic computation of the process of soot particle formation under conditions of the pyrolysis of hydrocarbons (in the C/H system) or for comparison of the numerical results with experimental data. This comparison is the strongest test for theoretical hypotheses of soot formation mechanisms.

Thus, the two currently available theories of soot formation consider two different families of molecules (polyynes and PAH) as gaseous precurrors of soot. Despite the fact that the hypothesis of the aromatic route to soot is presently predominant in the literature, experimental facts that are contradictory to this hypothesis have been accumulated in recent studies. In particular, an important step toward the elucidation of the chemical structure of the material of primary condensed particles was made in a series of papers [23, 29, 30]. It was found that primary condensed particles with an average size of 4–6 nm are transparent in the visible range of wavelengths and absorb with fluorescence in the near-UV range. Hence, it was concluded that these particles consist of small aromatic fragments coupled by aliphatic or perhaps oxygen bridges, and these fragments include no more than two or three condensed aromatic rings. Measurements [23] showed that the volume fraction and concentration of these species are close to the respective characteristics of a soot aerosol, which is detected downstream in a flame. The kinetic mechanism of formation and growth of transparent particles is unclear and cannot be explained on the basis of

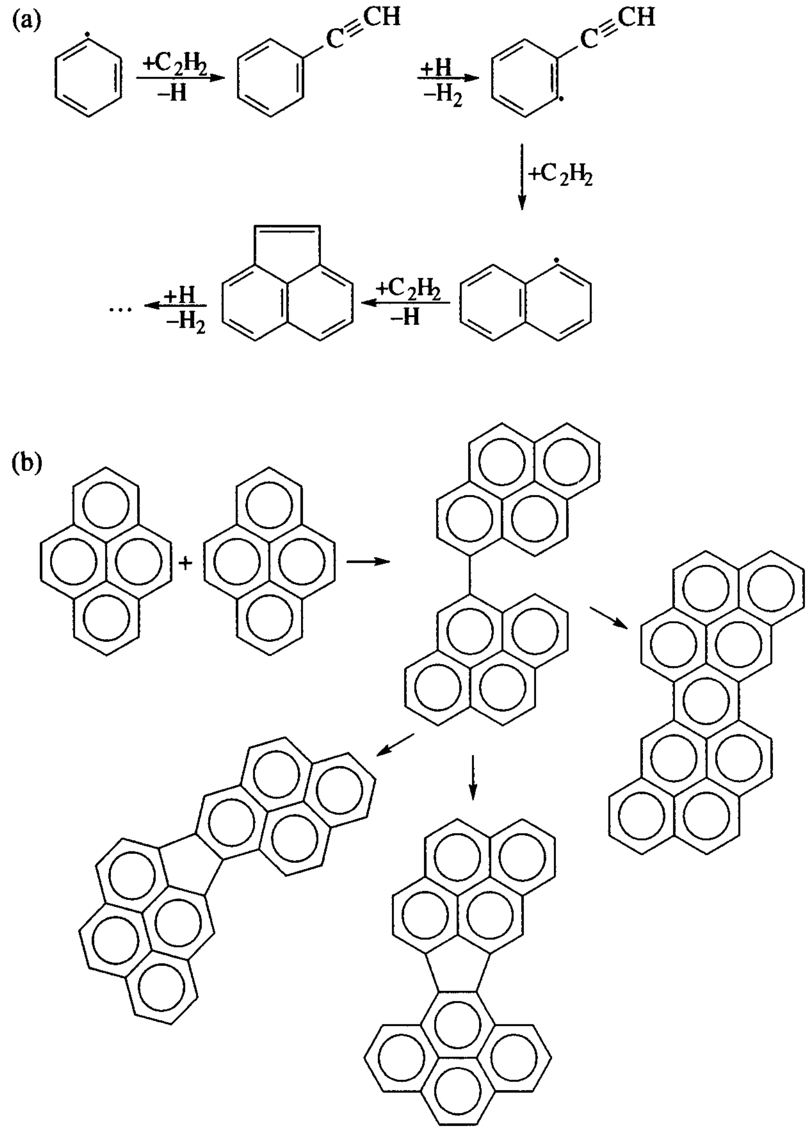

Fig. 3. Possible routes of the growth of polycyclic aromatic molecules: (a) mechanism of H elimination–C_2H_2 addition [14]; (b) polymerization of aromatic components [24].

existing kinetic schemes of the formation of aromatic structures [30]. The authors refer to the mechanism of formation of these particles as the initial process of fast polymerization. Thus, the results obtained in these works show that condensed particles formed in the soot zone of a flame have an initial structure which cannot result from the coagulation of large PAH molecules, as was suggested earlier [16]. Tesner *et al.* [31] came to a similar conclusion as a result of examining the soot formation in the pyrolysis of hydrocarbons from entirely different considerations. It was found that the particle concentration of soot in the pyrolysis of the mixture of naphthalene and acetylene is much lower (by a factor of 10 or higher at 1200°C) than that in the pyrolysis of only one aromatic compound. Because the addition of acetylene facilitates an increase in PAH concentrations [14, 32], these experiments show that PAH are not key compounds in the formation of soot nuclei.

The aim of this work is the comparative investigation of the processes of pyrolysis of benzene, acetylene, and diacetylene near a low-temperature threshold, when these hydrocarbons form a soot aerosol. At this low temperature, specific features of the initial molecular structure will maximally manifests themselves in the process of soot formation. It was reasonable to assume that the lower the temperature threshold of soot formation for a particular hydrocarbon (that is, the lower the potential barrier in the of soot aerosol formation from this hydrocarbon) the closer the structure and chemical properties of this hydrocarbon to the respective characteristics of yet unknown gaseous precursors of soot. We decided on hydrocarbons that play a key role in the existing hypotheses of the soot formation mechanism for our studies and a comparative analysis.

EXPERIMENTAL

Experiments on pyrolysis of hydrocarbons were carried out in a constant-temperature flow reactor. The design of the reactor was to a significant degree taken from [33, 34]. The schematic diagram of the experimental setup is shown in Fig. 4. The temperature profile in the reactor had an isothermal portion (within ±5 K) ~10 cm long. A hydrocarbon mixed with helium was injected into the beginning of this portion through a capillary 1 mm in diameter. The gas flow rate was 42 cm^3/s. Additional helium flow (8 cm^3/s) was supplied through the front end of the reactor for preventing the formation of dead zones. The average residence time of reactants in the isothermic zone (τ_R) at this flow rate was ~0.17 s. The influence of the reactor diameter on the experimental results was examined, because the experiments were carried out near the soot formation threshold. A reactor of diameter 20 mm was chosen as a reasonable compromise between a relative increase in the undesirable contribution of heterogeneous reactions at the walls of the reactor with a decreasing diameter, on the one hand, and, on the other hand, the deterioration of the temperature profile in the isothermal part of the reactor with the increasing diameter of the reactor. A flow rate of 50 cm^3/s assured the uniform removal of soot particles from the isothermal zone and, therefore, made possible the application, as a first approximation, of the model of a plug-flow reactor to the description of the chemical process in the reactor. Helium and acetylene were used in experiments without special purification; diacetylene was synthesized from 2-butyne-1,4-diol according to a procedure described in [35].

In the cases when the quantitative measurements were carried out, after completion of the process of pyrolysis, the condensed products were collected from the reactor walls and the filter and then washed in dichloromethane for the separation of soluble tar [20, 23]. The use of other solvents, for example, chloroform, changes to a certain degree the ratio between the amounts of carbonized products and soluble tar. Nevertheless, the form of functions remains identical in both cases, and the choice of a solvent does not influence the conclusions made in this work. The insoluble residue (carbonized products) consisted of soot particles and cokelike deposits on the reactor walls. These products were analyzed in all experiments simultaneously by optical and transmission electron microscopy. Near the threshold of soot formation, a considerable part of the soot formed remains in the reactor and cannot be separated from coke, because many soot particles are incorporated into the cokelike layer. An electron micrograph of an individual soot particle in the deposit at the reactor walls is presented in Fig. 5. Special scanning of samples was carried out for the determination of the lower limit of the pyrolysis temperature at which the first soot particles are formed.

We could not find any reasonable method for the determination of the threshold temperature of soot formation using the buildup curve of carbonized products (coke + soot), because near the threshold of soot formation, the relative contribution of coke to the total yield of condensed products is significant. Therefore, from here on, we consider the threshold temperature to mean a minimum temperature at which spherical carbonized particles that can be separated from the deposit at the reactor walls are detected. This moment was fixed by

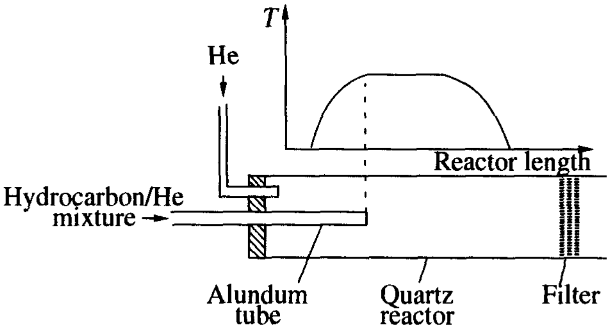

Fig. 4. Schematic diagram of the flow setup for the isothermal pyrolysis of hydrocarbons.

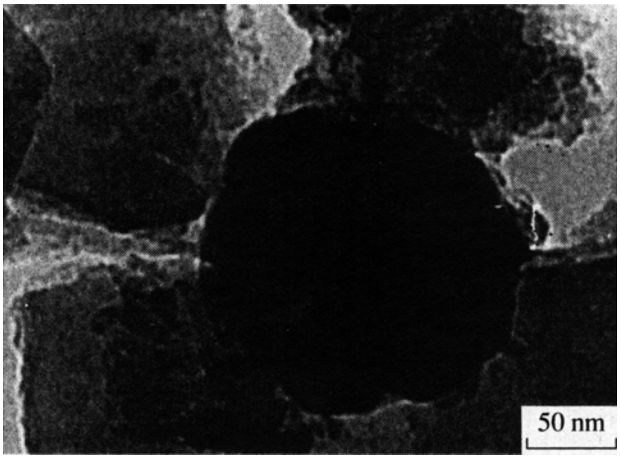

Fig. 5. Electron micrograph of a coke film on the reactor wall with an introduced soot particle.

means of an optical microscope by appearance of a typical suspension formed by spherical particles with a size of 0.3–0.5 μm in immersion oil. An NU-2 optical microscope (Carl Zeiss, Jena) was used for microscopic observation. Specimens were prepared by putting soot samples into a layer of immersion oil between intermediate and cover glasses. Observations and microphotographs were made in transmitted polarized and depolarized light. The spherical shape (Fig. 5) was considered evidence for the formation of these particles in a gas phase. The reactor temperature was changed from experiment to experiment by 15–20 K. This value is an error in the determination of the threshold temperature of soot formation.

The samples for electron microscopy were applied to a Formvar film support by sedimentation from a fluidized bed produced by ultrasound (35 kHz) in a dry state. No solvent was used. Observations and microphotographs were made on an HU-125 transmission electron microscope (Hitachi, Japan). Cokelike deposits were studied on the fragments obtained by grinding the initial material to desirable dimensions in an agate mortar.

Threshold temperatures of soot formation for hydrocarbons

Hydrocarbon	Concentration,* vol %	Time of pyrolysis, s	Temperature of soot appearance, K
Benzene	57 (9.5)	0.17	1230
Acetylene	27 (13.6)	0.17	1200
Diacetylene	9.2 (2.3)	0.17	800
Benzene	57 (9.5)	0.9	1100
Acetylene	27 (13.6)	0.9	1040
Benzene/acetylene	57/27 (9.5/13.6)	0.9	1070

* The concentration is expressed on the basis of the number of C atoms in a hydrocarbon molecule. The volume concentration of the hydrocarbon is given in parentheses.

RESULTS AND DISCUSSION

The data on the relative yield (on the basis of the initial carbon) of carbonized products (soot + coke) and tar (soluble part) as a function of the temperature of pyrolysis of acetylene, benzene, and diacetylene are presented in Figs. 6–8. In all cases, the first soot particles appeared at a temperature (marked by an arrow) at which an intense increase in the yield of carbonized products begins. The threshold temperature depends on the residence time in the reactor and on the hydrocarbon concentration. Therefore, this temperature is not an absolute characteristic the capability of a hydrocarbon for soot formation, but it can be useful for comparative investigations. According to the data in Figs. 6–8 and the table, the threshold temperature of soot appearance from diacetylene (790–810 K) is lower by almost 400 K than that for acetylene (1200 K) or benzene (1230 K) at the same residence time in the isothermal zone. Note that the volume concentration of diacetylene (in terms of C atoms) is considerably lower than the concentrations of acetylene and especially benzene (see the table). We consider this fact as direct evidence for the very high capability of polyynes to form soot in comparison with any other hydrocarbons. Therefore, they should be studied in detail as possible gas-phase precursors of soot. These data are in agreement with recent measurements of the soot particle yield in the pyrolysis of diacetylene [36]. The concentration of soot particles was found to be higher by one order of magnitude than the concentration of these particles formed in the pyrolysis of acetylene, benzene, ethylene, and other hydrocarbons. Note that the study of the structure and morphology of soot obtained from acetylene, benzene, and diacetylene by electron microscopy did not reveal any considerable differences between the soot samples obtained by pyrolysis of these hydrocarbons [37]. X-ray microdiffraction showed that all samples lack a graphite structure, and the soot particle material is a carbonized polymer. All samples exhibited diffusion halos; the intensity maximums of these halos corresponded to interplanar distances of 4.6, 2.08, and 1.24 Å with a scatter of no higher than 4%, which indicates the structural similarity of the polymeric materials.

We detected, under the optical microscope, transparent soot particles and soot particles at different steps of carbonization in some soot samples obtained from acetylene at a pyrolysis temperature close to the threshold temperature of soot formation (residence time in the reactor $\tau_R = 0.9$ s, $T \cong 1070$ K). Analogous particles were found in soot samples from diacetylene, which were obtained near the threshold of soot formation at $\tau_R = 0.17$ s. These particles are too small for observation under an optical microscope (300–500 nm), and the samples exhibit low stability (transparent particles dissolve in immersion oil in several tens of minutes);

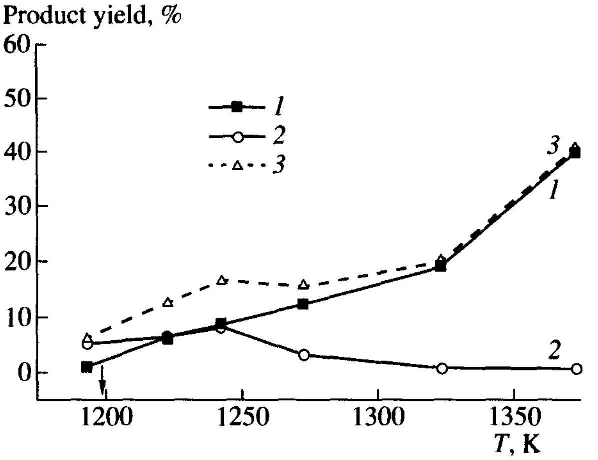

Fig. 6. The yields of condensed products of acetylene pyrolysis as a function of temperature: (*1*) coke + soot, (*2*) tar, and (*3*) the total yield. 13.6% C_2H_2–He mixture; $\tau_R = 0.17$ s. The arrow marks the threshold temperature of soot formation.

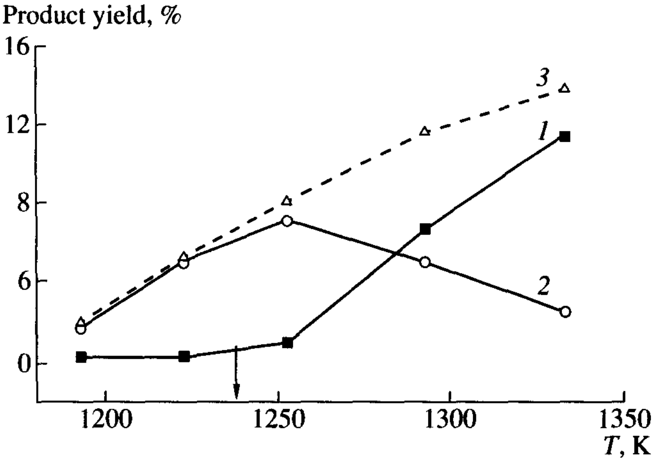

Fig. 7. The yields of condensed products of benzene pyrolysis as a function of temperature: (*1*) coke + soot, (*2*) tar, and (*3*) the total yield. 9.5% C_6H_6–He mixture; $\tau_R = 0.17$ s. The arrow marks the threshold temperature of soot formation.

thus, it is somewhat difficult to take photographs of these particles. Figures 9a and 9b present the samples containing transparent soot particles and particles of deeply carbonized soot. Transparent particles, which are optically active due to the crystal structure of polymeric materials, appear light against a dark background when observed in polarized light (Fig. 9c). Direct detection of transparent soot particles confirms the results and conclusions [14, 29, 30] on the low degree of aromaticity of the material of a primarily formed soot aerosol. That is, these particles cannot be a product of coagulation of bulky PAH components. The effective first-order rate constant of carbonization for soot particles formed in a diffusion ethylene flame was estimated in [38] to be equal to $1.8 \times 10^6\exp(-26.9/RT)$ (activation energy in kcal/mol). Therefore, at $T = 1070$ K, this constant is 5.6 s^{-1}, and the characteristic time of carbonization is comparable with the average residence time of reactants in the reactor in our experiments. This seems to be one reason for the possibility to observe both partially carbonized and noncarbonized aerosol particles in the samples.

For all three hydrocarbons, the yield of tar as a function of the pyrolysis temperature has a maximum which lies above the threshold temperature of soot formation. On this basis, supporters of the aromatic theory conclude that low-molecular-weight tar, which are mostly polycyclic aromatic compounds [19], are precursors of soot particles, and a decrease in their quantity is explained by their participation in the formation of soot material. However, the total yields of condensed products for acetylene and diacetylene also exhibit a maximum. In the latter case, this maximum is clearly pronounced and cannot be due to experimental error (Fig. 8). A deep crevasse in the curve representing the total yield of condensed products in experiments with diacetylene (at $T = 1020$–1070 K) cannot be explained by the loss of such a large amount of carbon in the course of carbonization of primary soot particles and coke. Indeed, according to all available data [21, 38, 39], the molar ratio C/H in soot particles is no lower than 2/1, and the main gaseous products of pyrolysis of diacetylene are methane and hydrogen [40]. Hence, it follows that the loss of condensed products in the reactions of carbonization cannot exceed 10–15 wt %, whereas in the experiments with diacethylene, a decrease in the total yield (tar + coke + soot) is 30–40% of the maximum value at $T = 970$ K. As can be seen from the graph (Fig. 8), this maximum in the curve presenting the total yield of condensed products of pyrol-

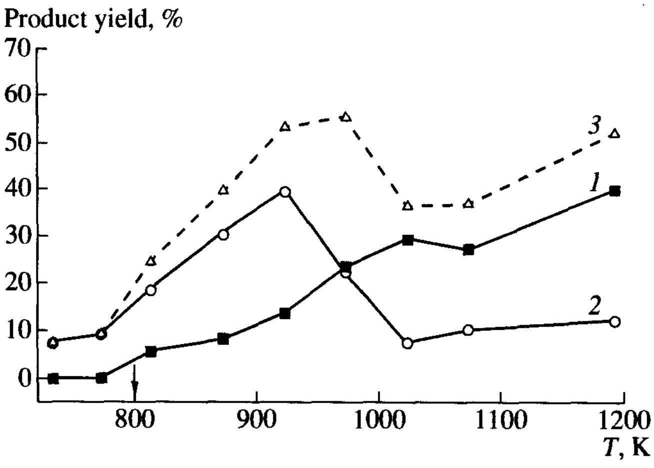

Fig. 8. The yields of condensed products of diacetylene pyrolysis as a function of temperature: (*1*) coke + soot, (*2*) tar, and (*3*) the total yield. 2.3% C_4H_2–He mixture; $\tau_R = 0.17$ s. The arrow marks the threshold temperature of soot formation.

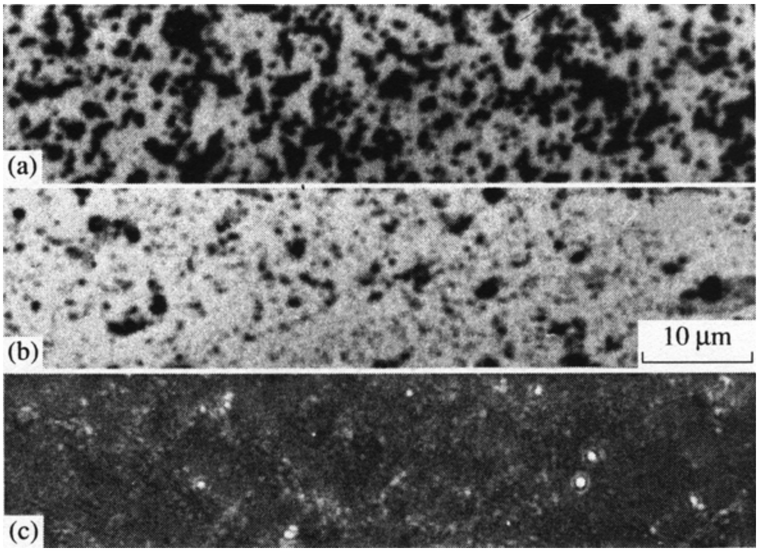

Fig. 9. Optical micrographs of soot particles (1700×): (a) opaque soot particles (2.1% C_4H_2/8.8% C_6H_6/He; 870 K; $\tau_R = 0.17$ s); (b) transparent soot particles at different steps of carbonization (transmitted depolarized light; 2.1% C_4H_2/8.8% C_6H_6/He; 810 K; $\tau_R = 0.17$ s); (c) the same sample as in (b), observation in polarized light.

ysis as a function of temperature is due to only the similar behavior of the curve representing tar yield. In contrast, the mass of carbonized products of pyrolysis (coke + soot) increases with temperature almost monotonically. Thus, the process of pyrolysis of diacetylene exhibits a number of interesting features concerning the mechanism of soot formation. This process is promising for further detailed kinetic study. For example, we can expect that two competing processes will be distinctly separated: the polymerization reaction leading to the formation of high-molecular aromatic products in a gas phase and the formation and growth of a soot aerosol. Probably, the reason for a dramatic decrease in the rate of the former process at 1000–1100 K is quite simple and results from the acceleration of the process of formation and carbonization of coke and soot. As a result of this, evolved hydrogen shifts the equilibrium $C_4H_2 + H_2 = 2C_2H_2$ toward acetylene, whose activity in the formation of tar and coke at this temperature is much lower (Fig. 6).

Comparison of the data presented in Figs. 6 and 7 shows that the threshold temperature of soot formation for acetylene (1200 K) is somewhat lower than for benzene (1230 K), whereas the volume concentration of benzene (in terms of C atoms) was deliberately chosen to be higher than that for acetylene. We carried out a series of experiments on the determination of the threshold temperatures for acetylene and benzene to obtain the final confirmation of this phenomenon. The total gas flow rate was diminished by a factor of five, but hydrocarbon concentrations remained unchanged. In this case, the residence time of the reactants in the isothermal zone increased up to 0.9 s. As a result, the threshold temperature of soot formation fell to 1040 and 1100 K for acetylene and benzene, respectively. Therefore, this experiment showed that near the low-temperature limit of soot formation, the ability to form soot in acetylene is higher than for benzene. At first glance, this fact seems odd because benzene has a much higher ability to form soot in flames. Neverthless, it is reasonable from the point of view of the acetylene route of soot formation. It was found only because we carried out our experiments near the low-temperature threshold of soot formation, where the products of thermal decomposition of benzene (first of all, diacetylene) were present in low amounts, and their contribution did not disturb the general pattern.

It also follows from the aromatic theory that a mixture of acetylene and benzene must have a threshold temperature of soot formation not higher (and, more probably, lower) than that of acetylene. This is due to the better conditions for the growth of polycyclic aromatic molecules in the mixture [14, 32]. We carried out experiments with the pyrolysis of a mixture containing 13.6% C_2H_2 and 9.5% C_6H_6 in helium. The residence time in the reactor was 0.9 s. We found that in this case, the threshold temperature is ~1070 K, that is, higher than the threshold temperature obtained in the pyrolysis of neat acetylene (1040 K). This result is in agreement with the data by Tenser and Shurupov [33], who showed that only acetylene participates in the formation of new soot particles in the pyrolysis of acetylene–benzene mixtures.

The measurement of threshold temperatures T_{gr} at different residence times in the isothermal zone τ_R permits us to find the temperature dependence of the induction period of soot formation from the equation

$$\tau_{ind}(T_{gr}) = \tau_R,$$

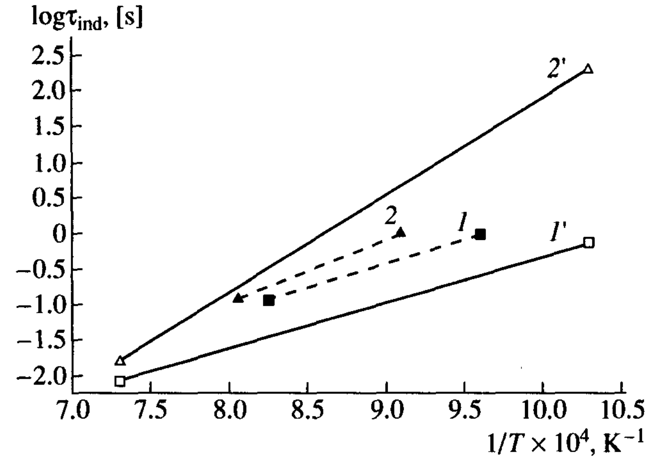

Fig. 10. Induction period of soot formation from (*1*, *1'*) acetylene (9.5% C_2H_2/He) and (2, 2') benzene (13.6% C_6H_6/He). (*1*, *2*) Estimation from the experimental data of this work; (*1'*, *2'*) extrapolation of the experimental data obtained in shock tubes for acetylene [41] ($T > 1650$ K) and benzene [42] ($T > 1500$ K).

if at least two pairs of (τ_R, T_{gr}) have been determined. Figure 10 shows the induction periods for acetylene and benzene, which were calculated from the experimental data for the residence times equal to 0.17 and 0.9 s (lines *1* and *2*, respectively). Solid lines (*1'*, *2'*) correspond to the values of τ_{ind} calculated by the extrapolation formulas suggested in [41, 42] on the basis of data obtained in shock tube measurements:

$$\tau_{C_2H_2} = 2.2 \times 10^{-12}[C_2H_2]^{-0.84}\exp(14700/T), \text{ s}$$

(concentration in mol/cm^3, [41], $T > 1650$ K),

$$\tau_{C_6H_6} = 7.8 \times 10^{-17}[C_6H_6]^{-0.75}\exp(31100/T), \text{ s}$$

(concentration in mol/cm^3, [42], $T > 1500$ K).

It can be seen in Fig. 10 that the induction period of soot formation from acetylene found in this work is lower than the corresponding value for benzene, although this difference is not very high, as indicated by the extrapolation of data measured in shock tubes.

CONCLUSION

1. The most important result of our experiments was the discovery of the very high capability of molecules with conjugated triple bonds and, particularly, diacetylene for the reactions of polymerization in a gas phase with the formation of high-molecular-weight products and a soot aerosol. The very high ability of diacetylene to form soot nuclei was found earlier [36]. Under typical conditions of enriched flames, the concentration of diacetylene is lower than the concentration of acetylene by approximately one order of magnitude [7] and remains lower than the thermodynamically equilibrium value under these conditions [20]. The concentration profiles of acetylene and diacetylene in the soot zone of the flame are similar in shape. This is indicative of a high rate of formation and consumption of diacetylene. The available kinetic mechanisms of thermal decomposition of acetylene [43] also indicate a high rate of formation of diacetylene and other polyynes under flame conditions. Therefore, the role of these molecules and, first of all, diacetylene in the formation and growth of a soot aerosol in flames can be considerable and is underestimated by the aromatic theory of soot formation.

2. Soot particles transparent in the visible region, which were detected for the first time in the processes of pyrolysis and particles at different steps of carbonization indicate that a soot aerosol is initially formed as a polymerization product of gas-phase molecules. The material of the particles consists of fragments with a small number of condensed aromatic rings. Then, after carbonization, these polymeric globules take the form of usual soot particles. This result is in complete agreement with the conclusions in [23, 29, 30], which were made on the basis of spectroscopic *in situ* measurements of primary condensed small particles (2–6 nm) and, therefore, raised doubts among a number of investigators.

3. Finally, considering our results together with the experimental data published in [23, 29–31, 33], we can conclude that all these data are in agreement with each other but do not support the aromatic hypothesis of soot formation. Our experiments also clearly demonstrated that the mechanism of polymerization of polyynes in a gas phase should be studied in detail both experimentally and theoretically from the standpoint of its contribution to the formation of a soot aerosol during the combustion and thermal decomposition of hydrocarbons.

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REFERENCES

1. Porter, G., *Proc. 4th Int. Symp. on Combustion*, Baltimore: Williams and Wilkins, 1953, p. 248.
2. Tesner, P.A., Gutor, I.M., Knorre, V.G., *et al.*, *Khim. Fiz.*, 1983, vol. 2, no. 8, p. 1103.
3. Von Helden, G., Hsu, M.-T., Gotts, N., and Bowers, M.T., *J. Phys. Chem.*, 1993, vol. 97, p. 8182.
4. Tomanec, D. and Schluter, M.A., *Phys. Rev. Lett.*, 1991, vol. 67, no. 17, p. 2331.
5. Krestinin, A.V. and Moravsky, A.P., *Chem. Phys. Lett.*, 1998, vol. 286, p. 479.
6. Bonne, U., Homann, K.H., and Wagner, H.Gg., *Proc. 10th Int. Symp. on Combustion*, Pittsburgh: The Combustion Institute, 1965, p. 503.
7. Bittner, J.D. and Howard, J.B., *Proc. 18th Int. Symp. on Combustion*, Pittsburgh: The Combustion Institute, 1981, p. 1105.
8. Cole, J.A., Bittner, J.D., Longwell, J.P., and Howard, J.B., *Combust. Flame*, 1984, vol. 56, no. 1, p. 51.

9. Krestinin, A.V., *Khim. Fiz.*, 1987, vol. 6, no. 3, p. 342.
10. Krestinin, A.V., *Advanced Computation & Analysis of Combustion,* Roy, G.D., Frolov, S.M., and Givi, P., Eds., Moscow: ENAS, 1997, p. 38.
11. Krestinin, A.V., *Khim. Fiz.*, 1998, vol. 17, no. 8, p. 41.
12. Krestinin, A.V., *Proc. 27th Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1998, p. 1557.
13. Warnatz, J., Behrendt, F., Sojka, J., *et al., Advanced Computation & Analysis of Combustion,* Roy, G.D., Frolov, S.M., and Givi, P., Eds., Moscow: ENAS, 1997, p. 64.
14. Frenklach, M., Glary, D.W., Yuan, T., *et al., Combust. Sci. Technol.*, 1986, vol. 50, p. 79.
15. Glassman, I., *Proc. 22nd Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1988, p. 295.
16. Harris, S.J. and Weiner, A.M., *Proc. 22nd Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1988, p. 333.
17. Wersborg, B.L., Horward, J.B., and Williams, G.C., *Proc. 14th Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1972, p. 929.
18. Wersborg, B.L., Yeung, A.C., and Horward, J.B., *Proc. 15th Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1974, p. 1439.
19. Homann, K.H., *Proc. 20th Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1984, p. 857.
20. Lam, F.W., Howard, J.B., and Longwell, J.P., *Proc. 22nd Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1988, p. 323.
21. Homann, K.H. and Wagner, Gg., *Proc. 11th Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1966, p. 371.
22. Tompkins, E.E. and Long, R., *Proc. 12th Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1969, p. 625.
23. D'Anna, A., D'Alessio, A., and Minutolo, P., *Soot Formation in Combustion,* Bockhorn, H., Ed., Berlin: Springer, 1994, p. 83.
24. Mukherjee, J., Sarofim, A.F., and Longwell, J.P., *Combust. Flame,* 1994, vol. 96, p. 191.
25. Miller, J.H., Smyth, K.C., and Mallard, W.G., *Proc. 20th Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1985, p. 1139.
26. Howard, J.B., *Proc. 23rd Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1990, p. 1107.
27. Frenklach, M. and Wang, H., *Proc. 23rd Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1990, p. 1559.
28. *Soot Formation in Combusion,* Bockhorn, H., Ed., Berlin: Springer, 1994.
29. D'Alessio, A., D'Anna, A., D'Orsi, A., *et al., Proc. 24th Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1992, p. 973.
30. Minutolo, P., Gambi, G., D'Alessio, A., and D'Anna, A., *Combust. Sci. Technol.*, 1994, vol. 101, p. 311.
31. Tesner, P.A., Evplanova, I.Ya., and Shurupov, S.V., *Kinet. Katal.*, 2000, vol. 41 (in press).
32. Lam, F.W., Longwell, J.P., and Howard, J.B., *Proc. 23rd Int. Symp. on Combustion,* Pittsburgh: The Combustion Institute, 1990, p. 1477.
33. Tesner, P.A. and Shurupov, S.V., *Combust. Sci. Technol.*, 1993, vol. 92, p. 61.
34. Tesner, P.A. and Shurupov, S.V., *Kinet. Katal.*, 1995, vol. 36, no. 4, p. 485.
35. Shostakovskii, M.F. and Bogdanov, A.V., in *Khimiya diatsetilena* (Chemistry of Diacetylene), Moscow: Nauka, 1971, p. 53.
36. Krestinin, A.V., Tesner, P.A., and Shurupov, S.V., *Kinet. Katal.*, 1998, vol. 39, no. 1, p. 5.
37. Raevskii, A.V., Krestinin, A.V., Kolesova, O.I., *et al.*, in *Khimicheskaya fizika protsessov goreniya i vzryva: XI simpozium po goreniyu i vzryvu* (Chemical Physics of Combustion and Explosion: XI Symposium on Combustion and Explosion), Chernogolovka, 1996, vol. 1, part 1, p. 52.
38. Dobbins, R.A., Govatzidakis, G.J., Lu, W., *et al., Combust. Sci. Technol.,* 1996, vol. 121, p. 103.
39. Haynes, B.S. and Wagner, H.Gg., *Prog. Energy Combust. Sci.,* 1981, vol. 7, p. 229.
40. Hou, K.C. and Anderson, R.C., *J. Phys. Chem.*, 1963, vol. 67, no. 7, p. 1579.
41. Frenklach, M., Taki, S., Durgaprasad, M.B., and Matula, R.A., *Combust. Flame*, 1983, vol. 54, p. 81.
42. Bauerle, St., Karasevich, Y., Slavov, St., *et al., Proc. 25th Int. Symp. on Combustion*, Pittsburgh: The Combustion Institute, 1994, p. 627.
43. Kiefer, J.H. and Von Drasek, W.A., *Int. J. Chem. Kinet.*, 1990, vol. 22, p. 747.