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IN MEMORY OF VLADIMIR EVGEN'EVICH FORTOV

Detonation wave of condensation

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<u>Abstract.</u> In a number of recent studies by the authors, a new physical phenomenon has been discovered and investigated in detail — the formation of a detonation wave during the condensation of highly supersaturated carbon vapor. The essence of the phenomenon is that an initiating shock wave propagating through an exothermic carbon compound (for example, carbon suboxide C_3O_2 or acetylene C_2H_2), as a result of its rapid dissociation, yields a highly supersaturated carbon vapor; the energy released during its condensation forms and maintains a detonation wave. This review describes in detail the results of experimental studies and their analysis based on the detailed kinetics and thermodynamics of the processes occurring and the one-dimensional Zeldovich–Neumann–Döring (ZND) theory of detonation. The potential to practically use the discovered phenomenon is discussed.

Keywords: detonation, shock wave, chemical condensation, carbon suboxide, acetylene, carbon, supersaturated vapor, nanoparticles, kinetics, thermodynamics

1. Introduction

Detonation is an extremely complex physical and chemical phenomenon based on the interaction among chemical,

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Received 26 November 2020, revised 16 January 2021 Uspekhi Fizicheskikh Nauk **191** (11) 1131–1152 (2021) Translated by V L Derbov thermodynamic, and gas dynamic processes. The phenomenon was first recorded and described at the end of the 19th century by a number of French scientists (Berthelot, Vieille [1], Mallard, Le Chatelier [2]) and almost simultaneously by Russian scientist Michelson [3]. The detonation theory was further developed by Chapman [4], Jouguet [5], and later by Zeldovich [6], Von Neumann [7], and Döring [8].

In the second half of the 20th century, interest in this phenomenon greatly increased from both the applied and fundamental points of view. In addition to a variety of original papers, a large number of reviews and monographs have been published reflecting the development of ideas about this complex phenomenon (see [9-14]). In applied research, besides the exploration of safety problems, the importance of which is continuously growing, at present, extremely intensive development is being carried out to create a detonation engine that could be a more efficient energy convertor than common combustion engines [15-18]. Finally, there is one more promising application of detonation, namely, the synthesis of nanodiamonds [19], as well as the synthesis and processing of other types of nanoparticles [20]. Therefore, alongside deeper studies of multiple aspects of detonation (overdriven and underdriven, spin and galloping, etc.), the search for new physical mechanisms capable of initiating a detonation, as well as various analogs of classical detonation initiated by exothermic chemical reactions in flammable and explosive substances, is an urgent issue. In particular, recently, the formation of 'light-induced detonation waves' generated by the effect of laser radiation has been predicted [21] and discovered [22].

In Ref. [23], another interesting analog of detonation was considered, the so-called detonation mechanism of normal phase propagation in superconductors with an electric current, when a high-power release of Joule energy generates a shock wave, at the front of which compression and irreversible heating of the substance destroy the superconducting state.

The process of condensation accompanied by a substantial heat release can be another attractive mechanism for initiating detonation. From the practical point of view, the heat release upon condensation can make a certain contribution to the detonation of gaseous hydrocarbons that dominates in practice and nature, since a majority of these processes involves the formation of condensed carbon particles [13, 24, 25]. On the other hand, it is necessary to emphasize that the analysis of detonation processes in hydrocarbon fuels typically misses the fact that the formation of condensed particles from the gas phase (condensation) is an exothermic process accompanied by a significant heat release. In particular, it is well known that the heat of carbon vapor condensation to graphite is about 720 kJ mol⁻¹. Therefore, a natural question arises: what is the role of this energy in the detonation of hydrocarbons? Moreover, if this energy is that large, is it possible to generate a detonation wave, maintained only by the condensation heat release?

When 12 years ago the authors first thought about this question, they expected the answer would most probably be negative, since the condensation process, in contrast to ignition reactions, is not accelerated with an increase in temperature, chain branching reaction mechanisms are absent, and the time of condensed particle growth can take a few million collisions.

Analysis of the literature did not inspire optimism either. In particular, Lev Landau had described the condensation jump arising during sharp expansion and cooling of a vapor in a supersonic jet [26] (Fig. 1). However, as Landau noted, with all its formal resemblance of a detonation wave, this jump does not transform a supersonic flow into a subsonic one, i.e., the condensation energy is not used to maintain the jump. At the shock adiabat (see Fig. 1), this jump corresponds to the segment A–O, shown by a dashed line. Such flow regimes are commonly called 'underdriven' or 'weak', i.e., unstable detonation, whereas the region of stable detonation lies above the point O. In other words, when describing the heat release upon condensation, Landau did not consider the situation in which the heat release initiates and maintains the shock wave.

Another luminary who dealt a great deal with the problems of detonation and condensation, Yakov Zeldo-

vich, also closely approached this problem, but he did not consider the possibility of the detonation wave of condensation either. It is remarkable that, when we first became interested in this problem, we closely collaborated with one more classic in the field of detonation and condensation of carbon nanoparticles behind shock waves, Heinz Wagner, from Göttingen.¹ Wagner told us that, many years ago, he discussed such a possibility with Zeldovich, but they both decided that the heat release rate due to condensation is insufficient to maintain a detonation wave (Fig. 2).

Moreover, considering a certain volume filled with an oversaturated vapor, it is impossible to formulate conditions for the propagation of a condensation wave. Indeed, if spontaneous condensation occurs at some point of this volume, it can only reduce the pressure, while the increase in temperature due to the condensation heat release at this point will reduce the oversaturation degree and, therefore, the condensation rate. Therefore, no conditions arise for the formation and propagation of a detonation wave, for which the necessary conditions are an increase in pressure and in sound velocity due to exothermic reactions (in classical detonation — due to the oxidation of a flammable gas).

However, a more careful analysis of the problem allowed formulating conditions for the appearance of a detonation wave of condensation. The basic condition is that the oversaturated vapor be produced by fast chemical reactions of decomposition of the initial gaseous substance behind the shock wave front. Thus, the shock wave must initiate the processes of formation of strongly oversaturated vapor, and its subsequent immediate condensation has to be accompanied by substantial heat release. Such a set of processes can be called chemical condensation, in contrast to the well-known 'physical condensation'. Indeed, in such a situation, the process of vapor formation due to dissociation of the initial molecules will exponentially accelerate with growing temperature, and the subsequent exothermic recombination reactions of condensation will provide fast and intense heat release. Obviously, the initial substance should be exothermic, i.e., the process of its pyrolysis and subsequent condensed phase formation should have a positive overall heat balance. The best-known compound of this type is acetylene. Acetylene pyrolysis yields graphitized soot and molecular hydrogen, and a significant amount of energy is released:

$$C_{2}H_{2} \rightarrow C_{2}$$

V

Figure 1. Landau condensation jump in a supersonic jet of oversaturated vapor [26].

$$C_2H_2 \rightarrow H_2 + \text{graphite} (+227 \text{ kJ mol}^{-1}). \qquad (1)$$





Ya B Zeldovich (1914–1987)

Figure 2. Zeldovich–Wagner: "It seems that the rates of condensation are too slow to support a detonation wave ..." (private communication).

¹ H Wagner passed away on July 29, 2020 during the preparation of this review, and we dedicate it to his memory.

Р



Pierre Eugene Marcellin Berthelot (1827–1907), a French physicochemist and organic chemist, historian of science, Foreign Corresponding Member of the Saint Petersburg Academy of Sciences (1876).



Henri Louis Le Chalelier (1850–1936), a French physicist and chemist, Foreign Corresponding Member of the Saint Petersburg Academy of Sciences (1913), Foreign Honorary Member of the Academy of Sciences of the USSR (1926).



Figure 3. Title page of issue 9, volume 129 of weekly reports (*Comptes rendus hebdomadaires des séances de l'Academie des sciences par mm. les secrétaires perpétuels*) of the sessions of the Academy of Sciences of France (August 28, 1899) and page 427 of this volume with the beginning of the paper [27] by Berthelot and Le Chatelier, "Sur le vitesse de détonation de l'acétylène" (On the Rate of Acetylene Detonation).

The detonation process upon spontaneous decomposition of acetylene was first observed already at the end of the 19th century by Berthelot and Le Chatelier [27] (Fig. 3): the measured velocity of the detonation wave increased from 1000 m s^{-1} to 1600 m s^{-1} , when the pressure before the wave increased from 10 to 30 atm. The authors of Ref. [27] emphasized that, to clarify the mechanism of detonation formation, it is necessary to consider a combination of chemical and thermodynamic processes. Since that time, of course, many authors have considered the detonation of acetylene. However, it appeared rather difficult to determine quantitatively the contribution of the condensation energy to the formation of a detonation wave in this process because of multiple complex intermediate reactions of the growth of polyatomic hydrocarbons that precede the formation of condensed carbon particles. Nevertheless, the high condensation heat of carbon vapors allows posing a natural question about the essential role of this energy in the detonation wave formation during the spontaneous decomposition of acetylene.

To determine the role of the condensation energy in the formation of a detonation wave in a clearer and quantitatively precise way, the authors of the present review proposed using another unique substance, carbon suboxide C_3O_2 . Carbon suboxide is a rather unstable volatile compound; when heated to 1400–1600 K, its molecules rapidly decompose into an atom of carbon and two CO molecules. The strongly oversaturated carbon vapor produced in this reaction immediately begins to condense into clusters and nanoparticles. The thermal decomposition of carbon suboxide in shock waves and the consequent formation of condensed carbon nanoparticles were studied in Refs [28–32]. The overall thermal balance of the process of transformation of carbon suboxide into condensed carbon and CO is also positive, although somewhat lower than in acetylene [29]:

$$C_3O_2 \rightarrow 2CO + \text{graphite} (+142 \text{ kJ mol}^{-1}).$$
 (2)

However, the fundamental difference between the condensation process in carbon suboxide pyrolysis and that in the pyrolysis of any hydrocarbons is that the carbon atoms and clusters are directly produced by its dissociation, whereas, in the pyrolysis of hydrocarbons, the formation of condensed carbon nanoparticles, as mentioned above, occurs via the consequent growth of polyhydrocarbon radicals with a decreased content of hydrogen atoms. Another important feature of carbon suboxide pyrolysis is that the limiting stage ('bottleneck') of the entire process, up to the formation of condensed particles, is the reaction of carbon vapor formation, the rate of which exponentially grows with an increase in temperature [28].

As known from Refs [33–35], at temperatures of 1800–2500 K and a pressure of 3–30 bar, the process of cluster growth to a size of $10^3 - 10^4$ atoms, accompanied by intense heat release, lasts only about 1–10 µs.

Thus, the analysis of data on the spontaneous decomposition of acetylene and shock wave pyrolysis of carbon suboxide provided certain prerequisites for the possibility of the existence of a fundamentally new form of detonation the detonation wave of condensation. Of course, this required setting up an entire series of special studies.

2. Experimental observation of the formation of a detonation wave of condensation in carbon suboxide

2.1 Exothermic properties of carbon suboxide pyrolysis

In the first series of studies aimed at precise measurements of heat release in the condensation of carbon nanoparticles, experiments were carried out in mixtures containing only 3% of C_3O_2 in argon [36, 37]. The experiments were performed behind reflected shock waves in a shock tube made of stainless steel with the inner diameter of 80 mm with a high-pressure chamber (HPC) 2.5 m long and a low-pressure chamber (LPC) 6.3 m long. The gas mixtures studied consisted of 3% C_3O_2 and 5% CO_2 in Ar. CO_2 was added to the mixture to increase the sensitivity of infrared (IR) thermometry, including the possibility of measuring the temperature before the beginning of particle formation. The pressure in front of the shock wave varied from 30 to 130 mbar. The initial parameters of the mixture immediately behind the shock wave front were determined by measuring the shock wave velocity based on signals from piezoelectric sensors. The



Figure 4. Schematic diagram of the setup and measurements of the growth of condensed carbon nanoparticles and the mixture temperature during the pyrolysis of carbon suboxide behind shock waves [37]. PEM — photoelectric multiplier, L_1-L_4 —lenses, SP—splitter plate.

resulting 'frozen' temperature T_5 of shock-heated gas behind the reflected shock waves was determined based on the onedimensional gas-dynamic theory and the assumption of vibration-rotational equilibrium and frozen chemical reactions. In experiments, the values of T_5 varied within the range of 1400–2200 K. The maximum time of measurements behind the reflected shock wave varied from 800 µs to 1000 µs, depending on the experimental conditions.

Figure 4 presents a schematic diagram of the setup and diagnostic instrumentation. The measurements were carried out in the cross section at a distance of 15 mm from the end of the shock tube. The formation and growth of the volume fraction of condensed particles was recorded by measuring the extinction of radiation from an He-Ne laser at a wavelength of 633 nm. To measure the temperature, a two-channel generalized spectral line reversal method [37, 38] was used, based on simultaneous measurement of emission and absorption in the IR spectrum at a wavelength of 2.7 µm (corresponding to the (1, 0, 1) vibrational absorption band of CO_2). The temporal resolution of the recording system was about 10 µs. The temporal profiles of the signals of emission $I_{\rm e}(t)$ and absorption+emission $I_{\rm a}(t)$ were independently recorded in two oscilloscope channels. The intensity of light transmitted through an absorbing medium is determined by the Lambert-Beer law and the correlation between the emissivity and absorption at any wavelength, by the Kirchhoff law for thermal radiation. A combination of these relations yields the temperature of the medium studied in the following form [38]:

$$T(t) = \frac{hv}{k_{\rm B}} \left\{ \ln \left[1 + \left(\exp \left(\frac{hv}{k_{\rm B}T_0} \right) - 1 \right) \right. \\ \left. \times \left(1 - \frac{I_{\rm a}(t) - I_0}{I_{\rm e}(t)} \right) \right] \right\}^{-1},$$
(3)

where $v = hc/\lambda$, k_B is the Boltzmann constant, and I_0 is the initial intensity of radiation from an etalon source. Such a

method is applicable only when the temperature of the medium is unchanged in the entire observation volume and the attenuation of probe radiation arises only because of absorption (rather than scattering). The first condition is fulfilled in the shock tube, if it is possible to ignore the boundary effects or sedimentation of cold particles on the windows. The second condition can be considered valid if the size of carbon particles is within the Rayleigh limits, i.e., the particle size is much smaller than the probe light wavelength. With an increase in the optical density of the mixture studied (i.e., at a high concentration of particles), the detection volume is shifted towards the detection window, which, however, is not important in a homogeneous mixture. However, in all experiments performed, the condition of an optically thin layer was satisfied (i.e., the absorption was < 10%).

Examples of signals obtained and the temporal profiles of the optical density of particles and current temperature of the mixture determined from them are presented in Fig. 5. The upper two rows of the oscillograms represent the emission signals, as well as the sum of emission and absorption, from which the mixture temperature was determined. The next two rows of the oscillograms demonstrate signals of extinction at wavelengths of 2.7 μ m and 633 nm. The bottom row of the oscillograms presents the profiles of the mixture temperature, determined using Eqn (3) from the upper two oscillograms. The extinction signal at the wavelength of 2.7 μ m was determined as the difference between emission and absorption-emission signals at the same wavelength.

Before the experiments with carbon suboxide, to check the temperature measurement technique, we performed a series of test measurements in nonreacting mixtures containing only 5% of CO₂ in Ar (Fig. 5a). The absence of extinction and good agreement between the measured temperature and the calculated 'frozen' temperature T_5 (dashed line in the bottom row of the plots in Fig. 5) are perfectly seen. The calculated error of temperature measurement depended on the difference between T_0 and T_5 and varied from ~ 20 K at $T_5 ~ T_0$ to ~ 50 K at $|T_5 - T_0| ~ 300$ K. The measurements in reacting mixtures (3% C₃O₂+5% CO₂ in Ar), presented in Fig. 5b–d, were carried out in the range of 'frozen' temperatures $T_5 = 1400-2200$ K (i.e., in the range where, in earlier papers [33, 34], the maximum optical density and particle size were observed).

At the lowest temperature, $T_5 = 1520$ K (Fig. 5b), both extinction signals grow after the end of the induction time in about 300 µs, which reflects the formation of particles. The measured temperature of the mixture agrees well with T_5 and remains constant for 700 μ s. Thus, in this case, neither C₂O₃ decomposition nor the formation of particles causes noticeable thermal effects. At $T_5 = 1743$ K (Fig. 5c), the extinction signals look similar, but the values of the measured temperature are close to T_5 only during the first 100 µs after the passage of the shock wave front. For $\sim 150 \ \mu s$, the temperature increases by ~ 150 K synchronously with a considerable increase in the extinction in the visible and infrared ranges. At $T_5 = 1985$ K (Fig. 5d), the extinction signals reflect a rapid growth of the particles. In this case, the measured temperature also shows values higher than T_5 by almost 300 K. During the remainder of the experiment, both the extinction and the temperature remain practically unchanged, which indicates the setting in of equilibrium in the mixture.

Thus, these preliminary experiments provided the first data about the substantial and sufficiently rapid heating of a



Figure 5. Examples of recorded signals (*U* is voltage), extinction temporal profiles evaluated from them at wavelengths of $\lambda = 633$ nm and 2.7 µm, and temperature in the mixtures of 5% CO₂ in Ar (a) and 3% C₃O₂ + 5% CO₂ in Ar (b-d) [36].

mixture containing only 3% of C₃O₂, which brought encouraging information about the possibility of forming a detonation wave upon the condensation of carbon vapors in this system. Here, it is necessary to emphasize again that the condition of major importance was that the entire process be limited by the rate of producing vapors of carbon or (in the case of hydrocarbons) active radicals, which are centers of subsequent condensation. This fundamental property of the chemical condensation provides an exponential acceleration of the entire process under an increase in temperature, which, in turn, is a necessary condition for the appearance and existence of a detonation wave. The experiments carried out allowed clarifying the fulfilment of this important condition. The obtained data on the temporal profiles of extinction provided information on the growth rate of the condensed phase volume fraction $f_{\rm V}$:

$$f_{\rm V} = -\frac{\ln\left(I/I_0\right)}{\varepsilon l}\,,\tag{4}$$

where I and I_0 are the intensities of the incident and transmitted radiation, respectively, l is the optical path length (the shock tube diameter), and ε is the extinction coefficient of carbon nanoparticles (for $\lambda = 633$ nm, $\varepsilon = 5.1 \times 10^6$ m⁻¹ [39]). The rate constant of the volume fraction of the condensed phase k_f was determined by extrapolating the late particle growth stages with the relaxation equation

$$\frac{\mathrm{d}f_{\mathrm{V}}}{\mathrm{d}t} = k_{\mathrm{f}}(f_{\mathrm{V}}^{\infty} - f_{\mathrm{V}})\,.\tag{5}$$



Figure 6. Effective rate constants of particle growth determined from measurements of extinction at 633 nm (circles) and temperature (triangles) [37]. Line shows the rate constant of C_3O_2 decay determined in Ref. [28].

The rate constants for the mixture temperature growth were determined in a similar way. In Fig. 6, data on the temperature dependences of the particle growth rate constants and the temperature of the mixture [37] are compared with those on the rate constant of C_3O_2 decay, measured in Ref. [28]:

$$k_{\rm d} = 2 \times 10^{15} \exp\left(-\frac{10720 \text{ K}}{T}\right) \, [\rm cm^3 \, mol^{-1} \, s^{-1}] \,.$$
 (6)

Good agreement among these dependences is seen, which confirms the fulfilment of the main condition of chemical condensation, the exponential increase in the rate of forming condensed particles with the growth of temperature.

Another important feature of carbon suboxide C_3O_2 decay and the subsequent condensation of carbon is the complete absence of secondary gaseous reactions (in the process of C_3O_2 dissociation, only carbon vapors and carbon oxide CO, which is chemically stable at temperatures T < 4000 K, stay in the system). This ensures the origin of the condensation wave immediately behind the zone of pyrolysis of the initial molecules.

The above properties of carbon suboxide pyrolysis made it possible to perform a simple analysis of the interrelation between the growth of condensed particles and the release of heat after shock waves of various intensities, which could allow estimating the threshold parameters for the formation of a detonation wave. To confirm the existence of this phenomenon reliably, changes in the condensation wave parameters were measured under various intensities of the initial shock wave and C_3O_2 concentrations.

2.2 Formation of a detonation wave of condensation

To clarify the interrelation between condensed particle growth and heat release after shock waves, the next series of experiments was carried out in mixtures containing 10-30% of C_3O_2 in Ar [40–43]. The temperature and pressure behind the reflected shock wave before chemical transformations (so-called frozen parameters) were in the ranges of 1400–2000 K and 4–9 bar, respectively. The actual pressure and velocity of the shock wave were measured with several piezoelectric sensors, located at distances from 0 to 300 mm from the

shock tube end. In addition, the intensity of radiation in the range $\lambda = 633 \pm 10$ nm and laser beam extinction, reflecting the formation of condensed particles, were recorded through different observation windows. Figure 7b, e, h shows the shock wave propagation in a mixture of 10% C₃O₂ + 90% Ar, when the frozen temperature behind the wave is $T_5 = 1390$ K and the measured wave velocity is $V_5 = 920$ m s⁻¹. At such a relatively low temperature, chemical transformations of C₃O₂ during the measurements are insignificant [29, 30] and the shock wave propagates with constant velocity and pressure, the emission and extinction being absent, except the sharp schlieren signal at the moment the shock wave front passes.

Figure 7c, f, i presents the experimental dependences observed in the same mixture of $10\% C_3O_2 + 90\%$ Ar, when the velocity of the reflected shock wave was $V_5 = 1040 \text{ m s}^{-1}$ and the frozen temperature was $T_5 = 1620$ K. At this temperature, the process of C₃O₂ decay and the formation of carbon particles is quite efficient, and it can be seen that, immediately after reaching the calculated pressure values behind the shock wave front, $P_5 = 4.5$ bar (dotted line), an additional increase in pressure reaching about 6 bar is observed. Further propagation of the shock wave is characterized by a noticeable increase in its velocity to $V_{exp} = 1290 \text{ m s}^{-1}$ and the appearance of a sharp peak of pressure immediately behind the front. These processes are accompanied by an increase in the height of emission peaks, which is evidence of a substantial temperature increase in a narrow zone behind the wave front. Figure 7i demonstrates the extinction growth reflecting the formation of condensed particles. Obviously, the condensation process also accelerates with the propagation of the shock wave.



Figure 7. (a) Schematic of shock tube and measurement windows, as well as temporal profiles of pressure (b–d), emission (*I* being signal intensity) at $\lambda = 633$ nm (e–g) and extinction of laser radiation (h–j), measured behind shock waves in mixtures of C₃O₂+Ar at distances of 70, 140, and 295 mm from the shock tube end. Mixtures and frozen temperatures T_5 behind the wave near the end: (b, e, h)—10% C₃O₂+Ar, $T_5 = 1390$ K, (c, f, i)—10% C₃O₂+Ar, $T_5 = 1620$ K, (d, g, j)—20% C₃O₂+Ar, $T_5 = 1440$ K. Characteristic times of increase in extinction [42] are indicated in Figs i, j.



Figure 8. (Color online.) Schematic diagrams of (a) additional section of the shock tube and multichannel diagnostics of detonation formation behind the reflected shock wave (RSW) by means of pressure sensors (S1–S4), temporal scans of emission using rectangular sapphire windows (W) and ICCD camera (C), as well as (b) measurements of laser extinction and flow's own emission using a continuous-wave He-Ne laser (L), system of mirrors (M), and PEMs (E1–E4 [42].

In mixtures containing 20% of C_3O_2 (Fig. 7d, g, j), a significantly greater acceleration of the shock wave from $V_5 = 1090 \text{ m s}^{-1}$ to $V_{exp} = 1490 \text{ m s}^{-1}$ was observed, accompanied by the formation of sharp pressure and emission peaks, as well as by jump-like condensation. It should be noted that the pressure and emission profiles, shown in Fig. 7d, g, are rather typical for gas detonation waves [11, 13, 14].

For the next series of experiments aimed at the continuous recording of the shock wave propagation process, the tube was equipped with a special additional section with two rectangular sapphire windows with the dimensions of 160×5 mm, the edge of which was located at a distance of 25 mm from the tube end. Through these windows, time-resolved images of the emission behind the shock wave in the range of 300–800 nm were recorded using an intensified charge-coupled device (ICCD) camera (StreakStar II, LaVision GmbH). In addition, the extinction of laser radiation at $\lambda = 633$ nm was recorded through the same windows at different distances from the tube end, which reflected the formation of condensed particles. Figure 8 presents a schematic diagram of the experimental setup and the basic diagnostic methods.

Figure 9 shows an example of a scanning record of the emission behind the shock wave obtained using the ICCD camera, as well as the pressure sensors in a test experiment with a mixture of 1% C₆H₆+Ar at temperature T_5 = 2800 K. Under these conditions, benzene pyrolysis and the formation of carbon nanoparticles occur very rapidly (in ~ 10 µs), and then no noticeable thermal effects are observed. Therefore, it is clearly seen that the wave propagates with constant velocity and the radiation field behind the shock wave is fairly homogeneous.



Figure 9. (Color online.) (a) Schematic diagram of the probing section of the shock tube with sapphire windows. (b) Example of temporary scan of emission behind the shock wave. (c) Records from pressure sensors in the test mixture of 1% C₆H₆+Ar at temperature $T_5 = 2800$ K. (From Ref. [42].)



Figure 10. (Color online.) Temporal scans of emission intensity behind shock wave front in mixtures initially containing different proportion's of C_3O_2 in Ar: (a) 10% C_3O_2 , $T_5 = 1650$ K, $V_5 = 1100$ m s⁻¹; (b) 20% C_3O_2 , $T_5 = 1530$ K, $V_5 = 1050$ m s⁻¹; (c) 30% C_3O_2 , $T_5 = 1490$ K, $V_5 = 1100$ m s⁻¹. Initial pressure behind reflected shock wave front in all experiments was 6 ± 1 atm [42]. Lines are the trajectories of the shock wave front plotted based on indications from pressure sensors (dots).

The ICCD camera records in the mixtures studied look quite different. Figure 10 shows the temporal scan of emission intensity behind shock waves in mixtures initially containing 10, 20, and 30% of C_3O_2 in argon. The frozen temperatures behind the front of a reflected shock wave in all cases are so low that no emission from the mixture before the heat release processes could be recorded. In the first case, in the 10% mixture, the most vivid picture of the gradual development of a detonation-like structure is observed. It is clearly seen how the condensation wave accompanied by emission overtakes the shock wave front in the middle of the window and accelerates the shock wave from $V_5 = 1050 \text{ m} \text{ s}^{-1}$ to 1300 m s⁻¹. In the mixture containing 20% of C₃O₂, in spite of the lower frozen temperature, the condensation wave overtakes the shock wave front much earlier. Immediately after that, a bright emission peak is formed at the front, and then a stable shock wave velocity of $\sim 1500 \text{ m s}^{-1}$ is observed (the initial value being $V_5 = 1025 \text{ m s}^{-1}$).

In the mixtures with 30% of C_3O_2 , the most surprising behavior of the shock wave is observed. First, it accelerates to 1600 m s⁻¹ (from $V_5 = 1100$ m s⁻¹), and then decelerates to 1300 m s⁻¹. The reason for such nonmonotonic behavior of the detonation wave of condensation upon an increase in the intensity of the initiating shock wave is the fundamental difference between the condensation kinetics and the kinetics of combustion processes. With an increase in temperature and approaching the temperatures of phase transition (sublimation) of the formed nanoparticles, the effective rate of their condensation inevitably decreases and, under certain temperatures, becomes less than the rate of their decay (disintegration) [31, 44]. According to the experimental data from Ref. [31] on the temperature dependences of growth and decay rates in carbon nanoparticles under carbon suboxide pyrolysis behind shock waves, the rate of particle growth begins to decrease at a temperature of about 2000 K, and at a temperature of 3000 K the particles begin to decay. Therefore, as the temperature in the condensation zone begins to approach these values, the process inevitably decelerates, which, in turn, leads to weakening and damping of the detonation wave.

2.3 Thermodynamics of shock-wave pyrolysis of carbon suboxide

To analyze in detail the thermodynamics of condensation processes under these conditions, the carbon nanoparticles formed were analyzed by means of X-ray spectroscopy and electron microscopy. The results show that the particles consisted of pure carbon and had a spherical shape $\sim 15-30$ nm in diameter (Fig. 11).

These data on the final size of the nanoparticles produced were used to analyze the process of heat release in the course of the observed phenomenon of chemical condensation, taking into account the obtained data on mixture heating during the thermal decomposition of C_3O_2 behind shock waves [36, 37]. Numerical calculations of C_3O_2 dissociation kinetics and subsequent condensation of carbon vapors with the energy balance of each reaction taken into account were carried out using the following kinetic scheme [28, 45, 46] (Table 1).

To perform quantitative calculations using this model, one should know the thermodynamic data of the formed clusters. The main uncertainty in the calculations was due to the absence of reliable data about the thermodynamics and enthalpies of the formation of carbon clusters and nanoparticles of different sizes. The thermodynamic data of the clusters from C_2 to C_{10} are known with a quite high degree of accuracy. The data on $C_1 - C_2$ were taken from Ref. [48], and on $C_3 - C_{10}$, from Refs [49, 50]. The properties of largesize clusters and nanoparticles, approximated by the method presented in Ref. [37], are summarized in Table 2.

The overall heat balance of the mixture Q as a result of the reaction

$$C_3 O_2 \to CO + \frac{C_N}{N} , \qquad (7)$$

where *N* is the number of atoms in a particle, was calculated using the formula

$$Q = \Delta H_{\rm f} \left(C_3 O_2 \right) - \Delta H_{\rm f} \left(CO \right) - \Delta H_{\rm f} \left(C_N \right), \tag{8}$$

where $\Delta H_{\rm f}$ are the enthalpies of formation of the mixture components.

Figure 12 presents the approximation of Q = f(N) using data from Refs [36, 37, 47–49]. According to the accepted values, the C₃O₂ dissociation energy (~ 573 kJ mol⁻¹) is completely compensated already at the cluster size of $N \approx 20$ atoms, and thereupon the process becomes exothermic.



Figure 11. Size distribution of carbon nanoparticles formed behind shock wave in a mixture of $20\% C_3O_2$ +Ar [41].



Figure 12. Overall heat balance of process $C_3O_2 \rightarrow CO + (1/N)C_N$ depending on the final size of particles N [41].

From Fig. 12, it is seen that, at a final particle size of 20 nm, which corresponds to $N \approx 10^6$ for the particle density of 1.86 g cm⁻³ [50], the heat release of the reaction approaches $\sim 120 \text{ kJ mol}^{-1}$.

Using these data, as well as that on the kinetics of C_3O_2 thermal decomposition, presented in Table 1, the calculated dependences of mixture heating because of carbon suboxide pyrolysis for 1 ms at various initial temperatures behind the shock wave were plotted (Fig. 13a). For comparison, Fig. 13b presents experimental data on the temperature dependence of the reflected shock wave velocity $V_{\rm R}$, measured in a 10% C₃O₂+Ar mixture at a distance of 195 mm from the end of the shock tube, as well as values of the wave velocity calculated for frozen conditions. The shock wave begins to accelerate at temperatures T > 1500 K, which correspond to the beginning of thermal decomposition of C_3O_2 [28]. At temperatures T > 2000 K, the difference among velocities reaches a maximum, which testifies to the contribution of the entire condensation energy to the shock wave dynamics. We note that the test experiments in nonreacting mixtures have shown very good agreement between the calculated and measured velocities of the reflected shock wave $(\Delta V_{\rm R}/V_{\rm R} \leq 0.01)$. Worth attention is the similarity of dependences in Figs 13a and b.

Table 1. Gas phase mechanism of thermal decomposition of C_3O_2 and formation of small carbon clusters.*

Reaction	A, cm ³ mol s	b	E, kJ mol ⁻¹	Reference
Thermal decomposition C ₃ O ₂				
$C + C_3O_2 \rightarrow C_2 + CO + CO$ $C + C_2O \rightarrow C_2 + CO$ $C_2O + C_2O \rightarrow C_2 + CO + CO$ $C_2 + C_2O \rightarrow C_3 + CO$ $C_2 + C_3O_2 \rightarrow C_3 + CO + CO$	$\begin{array}{c} 3.60 \times 10^{14} \\ 4.50 \times 10^{11} \\ 6.00 \times 10^{12} \\ 4.50 \times 10^{11} \\ 4.50 \times 10^{11} \end{array}$	0 0.5 0 0.5 0.5	23,000 0 23,000 0 85,000	[28] [28] [28] [29] [28]
Growth of small clusters				[45]
$C_n + C_2 O \rightarrow C_{n+1} + CO$	4.50×10^{11}	0.5	0	[28]
$S \leqslant n \leqslant 29$ $C_n + C_3 O_2 \rightarrow C_{n+1} + CO + CO$ 3 < n < 29	$4.50 imes 10^{11}$	0.5	85,000	[45]
$C_n + C \rightarrow C_{n+1}$ $1 \le n \le 29$	4.50×10^{11}	0.5	0	[28]
Thermal decomposition of small clusters				
$C_2 + M \rightarrow C + C + M$ $C_2 \rightarrow C + C$ $C_3 + M \rightarrow C + C_2 + M$ $C_3 \rightarrow C + C_2$ $C_4 \rightarrow C_2 + C_2$ $C_4 \rightarrow C_3 + C$ $C_5 \rightarrow C_4 + C$ $C_5 \rightarrow C_4 + C$ $C_6 \rightarrow C_5 + C$ $C_6 \rightarrow C_4 + C_2$ $C_6 \rightarrow C_3 + C_3$ $C_7 \rightarrow C_6 + C$ $C_7 \rightarrow C_6 + C$ $C_7 \rightarrow C_5 + C_2$ $C_7 \rightarrow C_4 + C_3$ $C_8 \rightarrow C_7 + C$ $C_8 \rightarrow C_6 + C_2$ $C_8 \rightarrow C_6 + C_2$	$\begin{array}{c} 1.22 \times 10^{12} \\ 2.90 \times 10^{15} \\ 1.22 \times 10^{12} \\ 1.90 \times 10^{16} \\ 3.60 \times 10^{16} \\ 5.60 \times 10^{15} \\ 1.10 \times 10^{16} \\ 2.20 \times 10^{16} \\ 1.10 \times 10^{17} \\ 4.20 \times 10^{17} \\ 1.20 \times 10^{17} \\ 1.20 \times 10^{17} \\ 1.00 \times 10^{18} \\ 2.40 \times 10^{18} \\ 1.10 \times 10^{17} \\ 3.90 \times 10^{18} \\ 2.20 \times 10^{19} \end{array}$	$ \begin{array}{c} -1 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0$	$\begin{array}{c} 1.34 \times 10^5 \\ 6.20 \times 10^5 \\ 1.84 \times 10^5 \\ 7.38 \times 10^5 \\ 5.78 \times 10^5 \\ 4.60 \times 10^5 \\ 7.00 \times 10^5 \\ 5.40 \times 10^5 \\ 5.88 \times 10^5 \\ 5.88 \times 10^5 \\ 3.10 \times 10^5 \\ 6.49 \times 10^5 \\ 5.37 \times 10^5 \\ 5.00 \times 10^5 \\ 5.31 \times 10^5 \\ 5.60 \times 10^5 \\ 3.30 \times 10^5 \end{array}$	[45] [46] [45] [45] [46] [46] [46] [46] [46] [46] [46] [46
$C_{8} \rightarrow C_{5} + C_{3}$ $C_{8} \rightarrow C_{4} + C_{4}$ $C_{9} \rightarrow C_{8} + C$ $C_{9} \rightarrow C_{7} + C_{2}$ $C_{9} \rightarrow C_{5} + C_{4}$ $C_{10} \rightarrow C_{9} + C$ $C_{10} \rightarrow C_{8} + C_{2}$ $C_{10} \rightarrow C_{7} + C_{3}$ $C_{10} \rightarrow C_{6} + C_{4}$ $C_{10} \rightarrow C_{5} + C_{5}$	$\begin{array}{c} 2.20 \times 10^{19} \\ 4.50 \times 10^{19} \\ 1.10 \times 10^{17} \\ 3.90 \times 10^{18} \\ 2.20 \times 10^{19} \\ 4.30 \times 10^{20} \\ 1.10 \times 10^{17} \\ 3.90 \times 10^{18} \\ 2.20 \times 10^{19} \\ 4.30 \times 10^{20} \\ 4.00 \times 10^{21} \end{array}$	0 0 0 0 0 0 0 0 0 0 0 0 0	$\begin{array}{c} 3.30 \times 10^{5} \\ 5.70 \times 10^{5} \\ 6.46 \times 10^{5} \\ 5.57 \times 10^{5} \\ 4.68 \times 10^{5} \\ 5.15 \times 10^{5} \\ 7.78 \times 10^{5} \\ 8.04 \times 10^{5} \\ 5.98 \times 10^{5} \\ 7.86 \times 10^{5} \\ 5.94 \times 10^{5} \end{array}$	[46] [46] [46] [46] [46] [46] [46] [46]
Coagulation of small carbon clusters				
$C_2 + C_2 \rightarrow C_3 + C$ $C_2 + C_3 \rightarrow C_4 + C$ $C_n + C_m \rightarrow C_{n+m}$ $2 \le n, m \le 15$ * Bate constants of reactions are presented in the form <i>k</i> .	2.5×10^{14} 2.5×10^{14} 4.5×10^{12} $= 4T^{b} \exp\left[-F/(RT)\right] = 0$	0 0 0.5	74,900 74,900 0	[46] [46] [45]

Table 2. Thermal effects of the formation of condensed carbon particles in the pyrolysis of C_3O_2 [37].

$ \begin{array}{c} 1\\ 2\\ 10\\ 19\\ 60\\ 10^5\\ 10^6\\ Graphite \end{array} $	-573.4 -268.5 -28.6 -3.7 100.4 113.1 123.1 142.64	[47] [47] [48] [48] [49] [37] [37] [49]

2.4 Various regimes of detonation formation

The effect of the condensation energy contribution to the shock wave dynamics greatly depends on the actual growth time of the particles up to their final size. This time can be qualitatively estimated from the extinction profiles shown in Fig. 7i, j. It is seen that, with shock wave amplification (and an increase in temperature), this time reduces from 80 to 10 μ s. It was mentioned above that the reason for the apparent acceleration of condensation with an increase in temperature is that the limiting stage that determines the rate of the entire process is the reaction of carbon suboxide dissociation $C_3O_2 \rightarrow CO + C_2O$, all other reactions being faster. In experiments [37], it was shown that, at temperatures up to



Figure 13. Comparison of calculated heating of C_3O_2 +Ar mixture with observed acceleration of the shock wave [40]. (a) Calculated dependences of mixture heating as a result of carbon suboxide pyrolysis for 1 ms at various C_3O_2 concentrations at the initial temperature behind the shock wave. (b) Comparison of reflected shock wave velocity V_R (triangles) measured at a distance of 195 mm from the tube end with the values of V_5 (asterisks) calculated for the frozen condition. 10% C_3O_2 +Ar mixture.

T = 2200 K, the growth rate effective constant coincides by an order of magnitude with the C₃O₂ dissociation rate constant k_d (see Fig. 6). However, the process behaves this way until the back reactions of decay of clusters and nanoparticles come into action due to the temperature growth. In Refs [30, 31], it is shown that, upon an increase in temperature to 2800–3000 K, the rate of particle formation behind the shock wave decreases. At T = 3000 K, the total time of particle growth exceeds 100 µs, and at T = 3400 K the rate of decay (evaporation) of particles appears to be already higher than the rate of their formation [31]. Consequently, it is obvious that, in contrast to the classical detonation supported by combustion processes, this phenomenon should have an extremum in temperature, depending on the integral heat release, and, upon overheating, the process should become self-decaying.

To evaluate to what extent the observed regimes of propagation of chemical condensation waves can be described by the laws that govern classical detonation waves, we performed calculations of Chapman-Jouguet detonation regimes within the Zeldovich-Neumann-Döring (ZND) one-dimensional theory of detonation [10, 51]. We should note that, according to modern ideas, the application of one-dimensional ZND theory to describe real parameters of detonation waves is strongly limited by the two-dimensional effects that arise due to the finite ratio of a detonation cell and the size of the channel along which the detonation wave propagates [10, 13]. However, from this point of view, in the case of chemical condensation waves, it is natural to understand the size of a 'detonation cell' as the size of the zone where the formation of condensed nanoparticles occurs and active heat release is observed.

As was mentioned in the Introduction, under the conditions considered, the dissociation endothermic reaction of C_3O_2 pyrolysis is a 'bottleneck' of the entire process, and, as can be easily estimated from Eqn (6), its characteristic time at temperatures above 2000 K and pressures of a few atmospheres is less than 1 µs. Experimental data on the particle growth rate, obtained from extinction measurements at $\lambda = 633$ nm (see Fig. 6), show that this process is even faster, its rate reaching ~ 10^{24} cm³ s⁻¹, which exceeds the rate of atomic collisions in carbon vapor and can be explained by a substantial contribution of the coagulation of growing carbon clusters. Qualitatively, these data are confirmed by the results of numerical calculations of the cluster growth rate using the kinetic scheme shown in Table 1. If the sound velocity in the zone behind the shock wave is of the order of 1 km s^{-1} , then the width of the reaction zone does not exceed 1 mm, which is substantially less than the diameter of the shock tube in which the measurements were carried out (80 mm). Therefore, the use of the one-dimensional ZND approximation could be considered fully justified for the rough estimates carried out.

The calculation results demonstrated reasonable agreement between the experimental data and the calculated parameters of classical detonation waves. Figure 14 illustrates a comparison of the observed parameters of chemical condensation waves with the behavior of Hugoniot adiabats [10, 51] for the initial mixtures (curves I) and for the mixtures after condensation (curves II). Straight lines 2–5 correspond to the calculated velocity V_5 of the reflected shock wave before the beginning of chemical transformations. Points 6 and rays 2–6 represent the measured maxima of pressure and the shock wave front velocity. Points P_{exp} show the established values of pressure, and point C–J corresponds to the Chapman–Jouguet detonation parameters calculated in the one-dimensional ZND approximation [51].

It is seen that, in the 10% C_3O_2 +Ar mixture (Fig. 14a), ray 2–6 crosses adiabat II at pressure P_{exp} , lying substantially higher than the C–J point, and the measured velocity of the wave is somewhat greater than the Chapman–Jouguet velocity (the tangent to curve II from point 2). Such a behavior of the wave may be caused by insufficient heat release, which leads to a continuation of maintaining the wave propagation by the pressure of the gas compressed near the tube end behind the wave front. Such a flow regime is usually referred to as 'overdriven detonation' [10].

In the mixture of 20% C_3O_2 +Ar (Fig. 14b), very good agreement between the measured and calculated values of pressure and wave velocity is observed. Under these conditions, the calculated temperature behind the detonation front is 2460 K, which, according to Refs [31, 33–35], corresponds almost to the maximal condensation rate. This fact is clearly demonstrated by the extinction profile in Fig. 7j.

In the richer mixture of 30% C₃O₂+Ar (Fig. 14c), the measured values of the pressure and velocity of the wave are



Figure 14. Behavior of Hugoniot adiabats for initial mixtures (curves I) and for those after condensation (curves II). Mixtures and temperatures are (a) 10% C_3O_2+Ar , $T_{C-J} = 2050$ K; (b) 20% C_3O_2+Ar , $T_{C-J} = 2460$ K; (c) 30% C_3O_2+Ar , $T_{C-J} = 2830$ K [41].

lower than the calculated detonation parameters. This fact can be explained by the excess heat release leading to incomplete condensation at temperatures above 2800 K. At such temperatures, the processes of particle decay that reduce the effective rate of condensation begin to play a considerable role. Due to these processes, the condensation energy cannot be completely transferred to the wave dynamics, and the socalled regime of damped 'underdriven' detonation is observed.

Thus, studies performed in mixtures containing the carbon suboxide convincingly showed that there are conditions under which only the energy of carbon nanoparticle condensation forms and maintains the detonation wave. In this case, the parameters of the detonation wave of condensation are described quite well within the classical onedimensional ZND theory of detonation.

3. Detonation wave of condensation in acetylene

3.1 Conditions for detonation in acetylene

From the results of studies performed in carbon suboxide, it followed that the heat release process in the course of carbon condensation should play a certain role in the detonation of most hydrocarbon fuels, which is accompanied by the formation of carbon nanoparticles. Acetylene is the most vivid example of a hydrocarbon capable of detonating without an oxidant, i.e., with the formation of condensed carbon. Indeed, acetylene is a unique exothermic hydrocarbon compound. As was mentioned in the Introduction, in the process of acetylene pyrolysis, graphitized soot and molecular hydrogen are produced and an energy of 227 kJ mol⁻¹ is released (see Eqn (1)). This substantially exceeds the heat release in the decomposition of C_3O_2 (see Eqn (2)) and is close to the heat release in the oxidation of hydrogen (242 kJ mol⁻¹).

Due to substantial heat release, the spontaneous decomposition of acetylene can occur in the regime of both deflagration with velocities from 10 to 50 cm s⁻¹ and detonation with a velocity up to 2000 m s⁻¹ [52]. Acetylene detonation was observed and studied in a number of papers (see, e.g., [25, 52–55]). The Chapman–Jouguet parameters the velocity and temperature behind the detonation wave in acetylene are well known [52]. From previous studies, it was also known that the detonation wave is formed only under sufficiently high pressures (as a rule, values above 10 bar are mentioned [52]). However, no detailed analysis of the condensation energy contribution to the formation of a detonation wave in acetylene was carried out before our work. Therefore, with the use of data on the condensation heat of carbon nanoparticles and the formation of a detonation wave obtained in carbon suboxide, an analogous study was undertaken for the formation of a detonation wave in acetylene.

Figure 15 presents emission records obtained using an ICCD camera in acetylene at various initial pressures [56]. For comparison, Fig. 15a shows a record obtained in a similar mode for C_3O_2 . The obtained data show that, in experiments performed under conditions similar to those in experiments with mixtures containing carbon suboxide, in mixtures with acetylene no detonation wave is formed, in spite of higher heat release. It is clearly seen that, in acetylene at an initial pressure of 6 atm and temperature of 1582 K (Fig. 15b), the condensation wave, clearly detected by intense heating of the mixture, is separated from the shock wave front by a rather wide zone (about 50 mm), which does not really change in time within the region of observation. In other words, under these condition, the condensation wave exerts no significant effect on the initiating shock wave, which continues propagating with constant velocity. Attempts to increase the shock wave velocity and to raise the initial temperature behind the shock wave to 2900 K did not result in any noticeable change in the shock wave behavior. However, upon increasing the pressure in the same mixture to 30 atm, even at the much lower temperature of 1312 K behind the initiating shock wave (Fig. 15c) the situation drastically changes. The condensation wave overtakes the shock wave, accelerates it, and forms a detonationlike structure with peaks of emission and pressure at the front, highly similar to those observed in C₃O₂ under a pressure of 7.5 atm (Fig. 15a).

To check the correspondence of the observed flow regimes to the parameters of detonation waves in the mixtures studied, we performed estimates based on the one-dimensional ZND detonation theory [10, 51], as was done above for detonation waves of condensation in carbon suboxide. Figure 16 illustrates a comparison of the observed parameters, namely, the wave velocity and the pressure behind it,



Figure 15. (Color online.) Comparison of intensity scans behind the shock wave front in mixtures initially containing 20% C₃O₂ (a) and 20% C₂H₂ (b) in Ar at different pressures *P*: (a) 7.5 atm, (b) 6 atm, (c) 30 atm. Red line is trajectory of the shock wave front determined from indications of pressure sensors (green dots) [56].



Figure 16. Hugoniot adiabats and observed detonation regimes [56]. Curves I are adiabats for initial mixtures, curves II, for mixtures after condensation; (a) mixture 20% C_3O_2 +Ar, $T_{C-J} = 2460$ K; (b, c) mixture 20% C_3O_2 +Ar, $T_{C-J} = 2517$ K. Points 2—initial states of mixtures before the shock wave, points 5—frozen parameters behind the shock wave, points 6—peak pressures behind the accelerated wave, P_{exp} —stabilized pressures behind the detonation wave, C–J — Chapman–Jouguet parameters.

with the behavior of Hugoniot adiabats for the initial mixtures (curves I) and mixtures after condensation (curves II). Straight lines 2–5 correspond to the calculated velocity of the reflected shock wave. Points 6 and rays 2-6 represent the measured maxima of pressure in the peak and the velocity of the wave front after its acceleration. Points P_{exp} show the established values of the pressure: 9.7 atm in C₃O₂ and 45 atm in C₂H₂, and the points C-J demonstrate the Chapman-Jouguet detonation parameters, calculated in the one-dimensional approximation [51]. It is clearly seen that, in both mixtures, the measured detonation velocities coincide with the calculated Chapman-Jouguet velocities within the measurement accuracy. The calculated pressures equal to 8.9 atm in C_3O_2 and 48 atm in C_2H_2 differ from the measured ones by less than 10%. The results obtained testify to the fact that the limit pressures of detonation occurrence in acetylene appear to be substantially higher than in C₃O₂, in spite of the greater thermal effect of reaction (1) than that of reaction (2). The most probable reason for the difference between the detonation wave formation processes in C_2H_2 and C_3O_2 is the difference between their heat release rates, determined by the peculiarities of carbon condensation kinetics during the pyrolysis of these two substances.

3.2 Specific features

of chemical condensation kinetics behind shock waves

The main source of information about the condensation kinetics in the experiments performed were the temporal profiles of laser radiation attenuation signals I/I_0 , i.e., the ratio of the transmitted radiation intensity I to the incident intensity I_0 . The amplitude of these signals allows finding the condensed phase volume fraction f_V (4). The time variation of f_V determines two quantities: the period of induction of the condensation beginning τ and the effective rate constant of the condensation process k_f .

Figure 17 shows a typical temporal profile of the condensed phase volume fraction f_V in acetylene behind the shock wave, which is recorded near the end of the tube after shock wave reflection (i.e., before the beginning of the condensation wave formation). The peak at the instant the shock wave front passes is related to laser beam deflection by the density gradient. After the wave passes, a long period of induction is observed, defined as the interval between the shock wave front passage and the point of crossing of the tangent to the signal profile at the point of its maximal slope with the time axis. Then, a sharp growth of the condensed phase follows, whose rate constant is determined by approx-



Figure 17. Typical temporal profile of the condensed carbon volume fraction determined from the signal of attenuation of probe laser radiation (see Eqn (4)) under C_2H_2 pyrolysis recorded immediately after reflection of the shock wave from the tube end, and its processing [56] (ppm—parts per million). Mixture is 20% C_2H_2 +Ar. Temperature and pressure behind the shock wave are 1562 K and 6.21 atm. Inset illustrates determination of the rate constant of the growth of the number of particles by approximating late phases of the process with relaxation equation (5).

imating the late stages of the process with relaxation equation (5).

Figures 18 and 19 present the results of measuring τ and $k_{\rm f}$ in rich mixtures, containing 20–30% condensing molecules, in comparison with measurements carried out in more dilute mixtures. All data are relative to the total concentration of condensing carbon and presented in Arrhenius coordinates, depending on the initial temperature behind the shock wave without considering thermal effects of the pyrolysis and condensation processes.

Figure 18 presents periods of induction in mixtures containing 20-30% acetylene and C₃O₂. It is seen that all results obtained in rich mixtures are in good agreement with measurements in more dilute mixtures, but what is of major importance is that the period of induction of particle growth in C_2H_2 in the entire range of measurements appears to be greater than in C_3O_2 by almost two orders of magnitude. Data on the condensation rate look quite different (see Fig. 19). In this case, the rates measured in rich mixtures taken relative to the initial temperature behind the shock wave turn out to be substantially higher than those measured in lean mixtures. Moreover, it is seen that the measured rates of condensation in acetylene are slightly lower that in C_3O_2 . The reason for the discrepancy with the data on lean mixtures can be attributed to considerable heating of the mixture at this stage of the process.

Indeed, the most important difference between the mechanism of condensed carbon formation in the pyrolysis of the hydrogen-free C_3O_2 precursor and soot formation in the pyrolysis of any hydrocarbons is that the primary products of C_3O_2 decay are directly the carbon atoms and radicals (see Table 1). Therefore, further growth of carbon clusters and the formation of condensed nanoparticles begin directly with the reaction of pyrolysis and occur either through surface growth,

$$\mathbf{C}_n + \mathbf{C} \to \mathbf{C}_{n+1} \,, \tag{9}$$



Figure 18. Measured induction periods in C_2H_2 (dark dots) and C_3O_2 (dark triangles) [56] in comparison with data for more dilute mixtures: squares $-5\% C_2H_2$ [57]; circles $-2\% C_2H_2$ [59]; diamonds $-10\% C_2H_2$ [60]; light triangles with point up $-(0.03-1\%) C_3O_2$ [29]; solid curve - approximation of data for acetylene-rich mixtures. (Concentration of carbon [C] is given in units of [mol s m⁻³].)



Figure 19. Condensation rate constants measured in C_2H_2 (dark dots) and C_3O_2 (dark triangles) [56] in comparison with data for more dilute mixtures (0.03–3%) C_3O_2 (light triangles) [29] and (0.2–1%) C_2H_2 (circles) [58]. Horizontal arrows indicate the possible shift of the real temperature of the mixture because of condensation thermal effects. (Concentration of carbon [C] is given in units of [mol s m⁻³].)

or through the coagulation of small clusters,

$$\mathbf{C}_n + \mathbf{C}_m \to \mathbf{C}_{n+m} \,, \tag{10}$$

with rates comparable to that of gas kinetic collisions [43].

In contrast to the pyrolysis of C_3O_2 , the pyrolysis of acetylene, as well as of any other hydrocarbons, does not directly lead to the appearance of carbon clusters. For example, Ref. [61] considers the reaction of H atom separation,

$$C_2H_2 + M \to C_2H + H + M, \qquad (11)$$

or the polymerization of C_2H_2 ,

$$C_2H_2 + C_2H_2 \to C_4H_3 + H$$
, (12)

to be primary reactions of acetylene pyrolysis, depending on pyrolysis conditions.

In further reactions, complex hydrocarbon radicals produce either polyacetylenes [62, 63] or polyaromatic structures [63, 64].

The analysis of general regularities in the formation of condensed particles during the pyrolysis of various hydrocarbon compounds behind shock waves allowed formulating a rather simple and clear physical model to describe the kinetics of chemical condensation [65, 66]. The model is based on two fundamental assumptions. First, it was assumed that the volume fraction of the condensed phase remains unchanged, starting from the temperatures that correspond to a complete release of carbon from the initial carbon-containing molecules (1600-2000 K) up to the temperatures of condensed carbon evaporation (sublimation) (which are from 3000 to 3500 K, depending on nanoparticle size). This assertion of the model relies on the well-known facts concerning the loss of thermodynamic stability in all hydrocarbon compounds at temperatures above 2000 K and on the carbon phase diagram, according to which it should be in a condensed state up to temperatures not exceeding 3000 K, as well as on experimental measurements of the temperature dependence of the volume fraction of particles [34, 35, 67].

The second basic assumption is that the growth (increase in size) of particles in the process of pyrolysis behind shock waves is completely determined by surface growth mechanisms, i.e., processes of recombination of small gas radicals (C atoms, small $C_2 - C_n$ clusters, etc., as well as hydrocarbon radicals C_nH_m , where $n \le 6$) on the surface of growing particles. It is well known that surface growth reactions are barrier-free and their rate is determined by the rate of gas kinetic collisions,

$$z = N_{\rm R} \sigma_{\rm p} v_{\rm R} \,, \tag{13}$$

where $N_{\rm R}$ and $v_{\rm R}$ are the concentration and thermal velocity of recombining radicals, and $\sigma_{\rm p}$ is the gas kinetic cross section of the particle. From this assumption, it follows that the condensation rate at a given concentration and particle size can increase upon temperature growth only as $T^{1/2}$, reflecting an increase in the thermal velocity of radicals.

The second assertion of the model has been clearly confirmed by data on particle size change under acetylene pyrolysis [67]. Figure 20 compares the time profiles of particle size measured at different temperatures. The coincidence of these profiles testifies that the rate of particle size increase remains practically unchanged with an increase in temperature, although, in accordance with the data from Refs [43, 58], the rate constant of the particle volume fraction growth k_f under acetylene pyrolysis and temperature growth from 1850 to 2050 K increases by about two times.

With these assumptions and an assumption that particles grow according to the surface condensation mechanism, the rate of increase in the number of atoms in a particle in the kinetic regime is determined by the relation [68]

$$\frac{dn}{dt} = N_{\rm R} \sigma_{\rm p} v_{\rm R} = N_{\rm R} n^{2/3} r_{\rm W}^2 \sqrt{\frac{8\pi k_{\rm B} T}{m_{\rm R}}}.$$
(14)

Here, $m_{\rm R}$ is the mass of atoms or active radicals taking part in the formation of particles, $r_{\rm W}$ is the Wigner–Seitz radius, and $k_{\rm B}$ is the Boltzmann constant. If the total growth time of particles $\tau_{\rm f}$ is known, then, disregarding the loss of atoms



Figure 20. Measured particle size growth during acetylene pyrolysis at temperatures of 1850 K (squares), 1950 K (dots), 2050 K (triangles) [67].

during this time, it is possible to determine approximately the final number of atoms in a particle or its size:

$$n_{\rm fin} \approx \left(\frac{8\pi k_{\rm B}T}{m_{\rm R}}\right)^{3/2} \frac{N_{\rm R}^3 r_{\rm W}^6}{27} \tau_{\rm f}^3 \,.$$
 (15)

Assuming that the total growth time of the particles can be estimated from experimental data on their growth rate constants [65, 66], we get

$$\tau_{\rm f}^{-1} \sim k_{\rm f} = A \exp\left(-\frac{E}{k_{\rm B}T}\right),\tag{16}$$

where *E* is the empirical value of the activation energy of the particle growth process, and, taking into account that for spherical particles $d \sim n_{\text{fin}}^{1/3}$, the temperature dependence of the particle size follows:

$$d(T) \sim \sqrt{T} \exp\left(\frac{E}{k_{\rm B}T}\right).$$
 (17)

Keeping in mind the condition of constancy of the final volume fraction of particles at different temperatures

$$f_{\rm V} = N n_{\rm fin} \frac{4\pi r_{\rm W}^3}{3} = {\rm const}\,,\tag{18}$$

as well as the relation

$$n_{\rm fin} \sim T^{3/2} \tau_{\rm fin}^3 \sim T^{3/2} \exp\left(\frac{3E}{k_{\rm B}T}\right),\tag{19}$$

it is possible to find the temperature dependence of the particle number density:

$$N = \frac{\text{const}}{n_{\text{fin}}} \sim T^{-3/2} \exp\left(-\frac{E}{k_{\text{B}}T}\right).$$
(20)

An important circumstance is that, in the process of surface growth, the number density of particles remains unchanged and reflects the number density of the condensation embryos. To clarify the physical meaning of dependence (20), the main processes determining the number density of condensation

Reactions of vapor or active radical formation	Activation energy E_d , kJ mol ⁻¹	$Model3E - (k_B T \ln T),kJ mol-1$
$\begin{array}{c} C_3O_2 \rightarrow C+2CO\\ 2C_2H_2 \rightarrow C_4H_3 + H \end{array}$	490 [28] 276 [70]	$\sim 620 [34] (> E_{\rm d})$ $\sim 300 [58] (> E_{\rm d})$

 Table 3. Comparison of temperature dependences of vapor (or active radical) formation rate with those in the model approximation.

nuclei (embryos) were considered. It is known that nucleation processes in highly oversaturated vapor are poorly described within the classical condensation theory; therefore, they should be considered based on the kinetic approach. The specifics of shock-wave pyrolysis are that the atoms or active radicals R_i participating in the nucleation process are formed by the dissociation of the initial molecules, which begins after the shock wave passage and has a rate constant described by the Arrhenius relation

$$k_{\rm d} = A \exp\left(-\frac{E_{\rm d}}{k_{\rm B}T}\right),\tag{21}$$

where E_d is the activation energy of the dissociation process. It is followed by the fluctuation growth of condensation embryos, which continues until they form clusters of critical size with the number density N. Since it is known in [29, 37, 69] that a 'bottleneck' of the entire process is exactly the reactions of dissociation of the initial molecules, and that the nucleation processes occur with high rates, it would be appropriate to accept the quasistationary approximation for estimating the concentrations of active radicals and critical embryos. In such a qualitative consideration, the steady-state concentration of seeds N is determined from the relation

$$N(T) = \frac{k_{\rm d}k_N}{2k_{\rm r}k_{\rm f}} \left[A\right] = \operatorname{const} T^{-1/2} \exp\left(-\frac{E_{\rm d}}{k_{\rm B}T}\right), \qquad (22)$$

where k_r is the rate constant of recombination of active radicals, and [A] is the concentration of the initial molecules [65]. Table 3 presents a comparison of the kinetic dependence (22) with the model relation (20) reflecting reasonable agreement between the proposed model and the experimental data. Note that the absence of exact agreement can be explained by the fact that, according to the model consideration (20) and kinetic relation (22), the growth of particles occurs at a constant temperature. In reality, in both substances considered, the pyrolysis is exothermic (see Eqns (1), (2)). In this case, the model number density of particles increases with temperature faster than the kinetic predictions, i.e., the process is self-accelerated due to heat release in the course of the reaction, which leads to an additional increase in temperature and -- under certain conditions-to the formation of a detonation wave of condensation.

Thus, the developed model made it possible, within the framework of simple and transparent assumptions, to describe the temperature dependences of chemical condensation behind shock waves, which provide the possibility of the formation of a detonation wave.

3.3 Energy balance at various stages of acetylene pyrolysis

The energy balance of all stages of pyrolysis of the initial substances and the formation of condensed particles are two more characteristics of primary importance that determine



Figure 21. Approximate dependences of the integral heat balance of the process $C_2H_2 \rightarrow H_2 + (2/N)C_N$ on the number of particles in a cluster *N* [43].

the possibility of the occurrence of a detonation wave of condensation. It is extremely difficult to calculate the energy balance of various stages of acetylene pyrolysis because of the huge number of intermediate stages of growth of polycyclic hydrocarbons, the thermodynamics of which are poorly studied. Figure 21 presents the approximate thermal balance dependences of acetylene pyrolysis on the size of the particles. The dependences Q = f(N) shown by dashed lines in Fig. 21 should be considered only as rough estimates of the thermodynamics of the process $C_2H_2 \rightarrow H_2 + (2/N)C_N$, by no means claiming to be correct in the region $2 < N < 10^3$. Two initial values of the dependences presented relate to two different primary reactions (11) and (12) of acetylene pyrolysis.

Thermal effects of the subsequent polymerization reactions are poorly known: it is possible only to indicate the rather high exothermicity of the process of 'folding' of linear acetylene radicals into a benzene ring [71]:

$$C_2H_2 \rightarrow \frac{1}{3} C_6H_6 (+200 \text{ kJ mol}^{-1});$$
 (23)

however, the discussion of how great the role is of such processes in acetylene pyrolysis has not yet yielded any definite conclusions [63, 64].

Anyway, it is possible to believe that growing polycyclic hydrocarbons gradually losing hydrogen atoms acquire the properties of carbon particles upon the relation $N_{\rm H} < 0.1 N_{\rm C}$ and $N_{\rm C} > 10^3$ (which corresponds to particle sizes of more than 1 nm). Exactly at such a size of the particles a substantial increase in their refractive index occurs, manifesting itself in a sharp increase in extinction at $\lambda = 633$ nm. The vertical arrow in Fig. 21 marks this region of particle size. The carbon particles free of hydrogen produced in the pyrolysis of C₃O₂ have a somewhat greater refractive index [29, 34, 72, 73]; therefore, the extinction begins to grow at smaller particle sizes.

In any case, complex hydrocarbon molecules produced at the considered stages of the acetylene pyrolysis process are most likely transparent to the probe laser at $\lambda = 633$ nm, and exactly this stage reflects the long period of induction in acetylene mixtures. Since the measured induction periods in the experiments considered, related to 'frozen' temperature T_5 , agree well with the data for dilute mixtures (see Fig. 18), we can conclude that the heat release at these stage of the process is still inessential, and the temperature of the mixture does not noticeably differ from the initial value of T_5 . Further stages of the process characterized by the formation of carbon particles, opaque at $\lambda = 633$ nm, indicate significant disagreement between the measured values of condensation rate constants and the data obtained for more dilute mixtures (see Fig. 19).

It is most natural to assume that the observed differences among particle growth rates in dilute mixtures is due to a substantial heat release at this stage of the process, leading to an increase in the mixture temperature. Simple estimates based on the integral thermal effects of reactions (1) and (2), as well as the approximate dependences, displayed in Figs 12 and 21, show that the temperature increment can reach more than 500 K in C_3O_2 and 800–1000 K in C_2H_2 .

The arrows in Fig. 19 show a shift in the values of $k_{\rm f}$ because of the increasing real temperature of the mixture. As can be easily seen, in this case, they would agree rather well with the data of measurements in lean mixtures.

From the presented consideration, it follows that the condensation rates in both mixtures are fairly high and the substantial heat release at this stage leads to an additional self-acceleration of the process.

Thus, we conclude that the main cause complicating the process of detonation wave formation in acetylene is not at all the differences among the condensation rates, but the long induction period not accompanied by noticeable heat release. This stage of the process spatially separates the shock wave front from the condensation zone, decreasing the influence of hot layers of the mixture on the shock wave parameters. Due to the insignificant activation energies of polymerization reactions, the rates of these processes weakly depend on temperature, but substantially increase with the growth of pressure. As a result, at an initial pressure of 6 atm behind the shock wave, in the region of observation, a nonstationary double-wave configuration exists consisting of a shock wave and the condensation wave following it (Fig. 15b). An increase in the pressure to 30 atm and, correspondingly, in the condensation of the reacting particles leads to a narrowing of the polymerization zone and an increase in the rate of its heating from the side of the heat release zone. The subsequent increase in the temperature gives rise to a sharp decrease in the induction period (see the solid curve in Fig. 18), apparently caused by including additional polymerization mechanisms with high activation energies. The collapse of the induction zone and joining of the heat release zone with the shock wave front, in turn, lead to the fast formation of a detonation wave.

4. Prospects for practical use of detonation wave of condensation

It is well known that the growth of energy consumption leads to an increase in the annual emission of CO_2 into the atmosphere by nearly 1.5%. This causes gradual climate warming, which in the near future may threaten us with serious environmental disasters. Therefore, all over the world, more environmentally-friendly methods of generating energy characterized by lower CO_2 emissions are being actively developed. From this point of view, the development of new energetic cycles using the energy of carbon condensation without its oxidation and formation of carbon dioxide is of special interest. Significant heat release characteristic of a detonation wave of condensation and the absence of carbon dioxide emission create favorable conditions for organizing a fundamentally new environmentally-friendly and efficient energy cycle. As early as 1940, Ya B Zeldovich showed that the cycle using the conversion of chemical energy via a detonation wave is the most advantageous from the point of view of energy efficiency [6]. The acetylene capability of oxygen-free decomposition with the formation of a detonation wave of condensation and an energy release of 227 kJ mol^{-1} can provide a high efficiency to power plants using the energy of a detonation wave of condensation.

In the recent paper [74], the first attempts were made to use the energy of condensation released in the process of acetylene self-decomposition to operate a combustion engine (CE) and a flow reactor. The experiments carried out demonstrated the possibility, in principle, of CE operation on undiluted acetylene; however, soot formation appeared to be the main problem, since the deposition of soot in the piston bank of the engine lead to its rapid halt. It was shown that the disadvantages of the piston system could be obviated by proceeding to a flow reactor with a continuous supply of fuel (acetylene) and the removal of reaction products (hydrogen and soot flow). A prototype of such a device was manufactured and tested. The results of experiments with a flow reactor with external heating to a temperature of 1000 °C have shown that the proportion of acetylene decomposition upon the consumption of 100 cm³ m⁻¹ increases with the growth of pressure, reaching 68% at 2 atm. Therefore, both tested devices testified to the prospects of developing and creating new types of environmentally-friendly energy generators, which could operate in a continuous mode using acetylene as the main fuel.

4.1 Schematic diagram of the energy cycle using acetylene condensation energy

The authors of Ref. [75] proposed a possible type of stationary device based on the process of acetylene detonation self-decomposition aimed at generating thermal and mechanical energy without using oxygen, which, moreover, can produce hydrogen and nanodisperse technical carbon. A general layout of such a setup must incorporate a detonation chamber, in which gaseous acetylene by detonation pyrolysis is transformed into a fast-moving high-temperature (about 2500 K) flammable mixture of detonation products: hydrogen gas and carbon nanoparticles (soot). With a 100% decomposition of acetylene into hydrogen and soot, an energy of 227 kJ mol⁻¹ is released at this stage of the setup's operation (see Eqn (1)).

The subsequent cycle of the setup's operation implies separation of carbon nanoparticles from hydrogen and combustion of the latter with the additional release of energy:

$$H_2 + 0.5O_2 \rightarrow H_2O (gas) + 241.7 \text{ kJ mol}^{-1}$$
. (24)

Thus, the ideal total energy yield of the proposed setup would be 468 kJ mol⁻¹. In this case, there is no emission of CO_2 and a large amount of valuable product, soot, is obtained which is used in various industries. Obviously, the real energy balance of such a cycle should consider unavoidable losses due to incomplete pyrolysis of acetylene, which can be determined only for a particular type of device. An energy generator based on the detonation self-decomposition of acetylene might be particularly desirable under anaerobic, e.g., submarine or space, conditions. In conditions on the ground, the



Figure 22. Design layout of an energy setup based on the detonation selfdecomposition of acetylene [75]: *1*—heat exchangers; *2*—acetylene vessel or generator; *3*—acetylene supply pipeline; *4*—waterlock; *5*—detonation chamber for decomposing acetylene oxygen-free; *6*—acetylene detonation initiator; *7*—separator of carbon nanoparticles; *8*—compressor; *9*—air supply pipeline; *10*—hydrogen combustion detonation chamber; *11*—initiator of hydrogen-air detonation; *12*—nozzle unit; *13*—turbine; *14*—turbine nozzle; *15*—connector between separator and reservoir for carbon nanoparticles; *16*—reservoir for collecting carbon nanoparticles.

addition of a second cycle with combustion of the generated hydrogen makes it possible to obtain a high energy yield in an environmentally-friendly manner.

An example of a possible design of such a setup is presented in Fig. 22. The ground-based energy setup operates as follows. Through a pipeline, the acetylene from a vessel or an acetylene generator is supplied to the first detonation chamber. The pipeline is equipped with a waterlock to prevent the penetration of a wave from acetylene detonation into the vessel or gas generator. Opening and closing the pipeline are implemented in the gas dynamic valve mode using pressure pulsations in the detonation chamber arising during the passage of the detonation wave. The parameters of gas dynamic valve (its main parameter being the ratio of the supply pipeline diameter to the detonation chamber diameter) are calculated based on the pressure on the detonation chamber wall and the pressure of acetylene flow at the chamber entrance. The first detonation chamber is equipped with an initiator of direct detonation of acetylene, located near the back open end. The initiation is executed periodically upon filling the chamber with a new portion of acetylene. The arising detonation wave moves to the closed end, leaving hot products of detonation behind it - hydrogen and fine-dispersed carbon, which expand towards the separator. In the separator, the carbon nanoparticles are separated from the gaseous hydrogen and collected in a reservoir. The hydrogen carried by the jet of air ejected into the chamber by a compressor is supplied to a second detonation chamber. A gas dynamic valve opens and closes the oxidant ejection pipeline. The hydrogen mixes with air along the chamber length. By means of the second detonation initiator located near the end of the second chamber, a detonation wave is periodically formed, which moves towards the chamber entrance to the air ejection location. Further upstream, the detonation wave fades because of the absence of the oxidant supporting the chemical reaction. Hot products from the detonation of hydrogen and air (water vapor and nitrogen) expanding in the nozzle enter the inlet of the electric generator turbine and drive it into rotation. The walls of the detonation chambers, acetylene generator, separator, bunker, and turbine outlet, heated in the course of operation, are equipped with heat exchangers,

in which the carrier is heated for further utilization of the obtained thermal energy.

In an anaerobic option of the energy setup, the second detonation chamber for hydrogen combustion and the turbine are removed. The energy setup will operate in the mode of generating thermal energy, carbon nanoparticles, and hydrogen due to the detonation decomposition of acetylene in the first detonation chamber.

4.2 On the possibility of promoting a detonation wave of condensation in acetylene with a methane admixture

From the point of view of practical implementation of the energy cycle described in Section 4.1, two important problems should be solved: to find ways to produce acetylene more cheaply and to reduce the limit pressure for the formation of detonation, which will allow creating safeer and more economical setups.

It is known that in practice one of the main technologies for acetylene production is the partial conversion of methane, in which the produced acetylene inevitably contains a small methane admixture [76, 77]. In contrast to acetylene, methane is a highly endothermic compound: its pyrolysis with the obtainment of condensed carbon proceeds with a great consumption of energy and is extremely difficult. Therefore, it would be natural to expect that the addition of methane to acetylene would suppress the process of self-decomposition and formation of a detonation wave of condensation.

However, in our recent papers [78, 79] it was experimentally discovered that small admixtures of methane promote the process of formation of condensed carbon nanoparticles in the shock-wave pyrolysis of acetylene. This effect was qualitatively explained by the appearance of new kinetic paths of growth for polyaromatic hydrocarbon compounds (PAHs) and the subsequent creation of condensed particles. The interaction of the methyl radical CH₃ (the primary product of methane pyrolysis) with acetylene molecules opens a path for the efficient formation of the propargyl radical (C₃H₃) that rapidly leads to the formation of the first aromatic ring, benzene C₆H₆ and phenyl C₆H₅, and further growth of PAHs:

$$CH_4 + M \to CH_3 + H + M , \qquad (25)$$

$$CH_3 + C_2H_2 \to C_3H_3 + H_2$$
, (26)

$$C_3H_3 + C_3H_3 + M \to C_6H_6 + M$$
, (27)

$$C_3H_3 + C_3H_3 \to C_6H_5 + H$$
, (28)

$$C_6H_6(C_6H_5) \rightarrow \ldots \rightarrow PAH \rightarrow \ldots \rightarrow nanoparticles$$
. (29)

It was mentioned above that the formation of a detonation wave of condensation in acetylene was observed only at sufficiently high pressures behind the initiating shock wave $(P \ge 30 \text{ atm})$ [56]. An analysis of the results obtained has shown that the main complication of the detonation wave formation in acetylene is the long stage of PAH growth not accompanied by a substantial heat release and, thus, separating the heat release zone from the shock wave front.

To analyze the kinetic mechanisms of the influence of methane admixtures on the pyrolysis and formation of a detonation wave of condensation in acetylene, a numerical study of the PAH and condensed carbon growth kinetics was carried out in Ref. [80], as was an analysis of time profiles of



Figure 23. Comparison of calculated temporal profiles of pyrene ($C_{16}H_{10}$) molar fractions (dashed lines *l* and *2*) and overall mass fraction of nanoparticles more than 2 nm in size (solid lines *3* and *4*) in acetylene (curves *l* and *3*) and a mixture of 90% $C_2H_2+10\%$ CH₄ (curves *2* and *4*). Initial temperature is T = 2000 K, pressure is P = 1 atm [80].

temperature and pressure variation under the shock-wave pyrolysis of acetylene, containing a small methane admixture (up to 10%).

The calculations were carried out with the program OpenSMOKE++ [81, 82] that uses the most up-to-date model of the growth of condensed carbon nanoparticles upon pyrolysis and oxidation of a wide spectrum of hydrocarbon fuels [83]. The model is based on the gas phase kinetic model of high-temperature pyrolysis and oxidation of hydrocarbon fuels, as well as on the discrete sectional approach to describe the nucleation of nanoparticles and the increase in the total mass and size of particles due to surface growth and coagulation. Heavy PAHs and nanoparticles of different sizes were subdivided into 20 pseudo-classes with a doubling of mass when going from one class to another. Each class included a fixed number of carbon and hydrogen atoms. The thermochemical properties of the classes were based on the group additivity method. This model was successfully tested for the conditions of high-temperature pyrolysis of acetylene [84]. The calculations were carried out in the zerodimensional approximation for a constant volume. The initial pressure and temperature in the calculation corresponded to the possible parameters behind the shock wave front immediately after its origin.

Figure 23 presents the calculated temporal profiles of the pyrene ($C_{16}H_{10}$) molar fraction and the overall mass fraction

of nanoparticles above 20 nm in diameter in acetylene and a mixture with a molar content of $90\%C_2H_2 + 10\%CH_4$ after isochoric heating of the mixture, imitating shock-wave heating. A substantial acceleration of the growth of PAHs and condensed particles upon the addition of methane is clearly seen

Figure 24 demonstrates the acceleration of an increase in temperature and pressure upon the addition of methane to acetylene under the same initial parameters behind the shock wave. From the presented data, it is obvious that the accelerated increase in pressure must inevitably lead to a faster formation of a detonation wave, as well as to a decrease in the threshold pressure for the origin of acetylene detonation in the presence of a methane impurity.

On the other hand, it is necessary to note that the admixtures of endothermic methane will inevitably lead to a certain decrease in the overall heat release and, respectively, to some lowering of the detonation wave of condensation parameters. Approximate estimates within the ideal one-dimensional detonation theory have shown that, for a mixture of 90% C₂H₂ + 10% CH₄ considered with initial temperature T = 300 K before the shock wave and pressure P = 1 atm, the Chapman–Jouguet parameters will be as follows: detonation wave velocity $V_{C-J} = 2001$ m s⁻¹, temperature $T_{C-J} = 3120$ K, and pressure $P_{C-J} = 20.33$ atm (instead of $V_{C-J} = 2033$ m s⁻¹, $T_{C-J} = 3214$ K, and $P_{C-J} = 20.88$ atm for 100% C₂H₂).

Thus, the results of calculations [80] have shown that, indeed, at temperatures above 1700 K and a pressure of P = 1 atm behind the shock wave front, an admixture of methane provides a substantial promotion of PAH growth and the subsequent growth of condensed particles, accompanied by an increase in temperature and pressure. For lower temperatures of the initial mixture, the promotion should be observed only at higher pressures. The results obtained indicate a possible decrease in the threshold pressure and acceleration of the development of acetylene detonation in the presence of methane admixtures, which, in practice, can noticeably improve the economy and safety of the proposed energy cycle that uses the energy of a detonation wave of condensation in acetylene.

4.3 Prospects for developing

an environmentally-friendly methane energy cycle

Another more general approach to the creation of an environmentally-friendly energy cycle is the development of devices operating on natural fuel. Indeed, acetylene is not a



Figure 24. Comparison of calculated temporal profiles of temperatures (a) and pressures (b) in acetylene (curves *I*) and in a mixture of 90% $C_2H_2+10\%$ CH₄ (curves 2). Initial temperature is T = 2000 K, pressure is P = 1 atm [80].

natural fuel, and its production requires a substantial energy expenditure. For example, the oxygen-free conversion of the natural fuel methane into acetylene and hydrogen,

$$2CH_4 \rightarrow C_2H_2 + 3H_2, \qquad (30)$$

requires an energy of about 376 kJ mol⁻¹.

Since process (30) generates 3 moles of hydrogen, which is also a perfect environmentally-friendly fuel, we can take into account the heat of its combustion (see (22)) $241.7 \times$ $3 \approx 725$ kJ mol⁻¹ and finally get an energy of 227 + 725 -376 = 576 kJ mol⁻¹ from two moles of methane, completely excluding the formation of carbon dioxide.

For comparison, recall that, in the direct combustion of methane,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O (gas), \qquad (31)$$

an energy of 802 kJ mol⁻¹ is released, i.e., the combustion of two moles of methane releases an energy of 1604 kJ mol⁻¹. Therefore, the 'energetic cost' of the environmentally-friendly energy produced in such a cycle (methane \rightarrow acetylene+hydrogen \rightarrow soot+water) will be more than three times the cost of the energy obtained with methane combustion.

On the other hand, if the aim of the energy cycle considered is not to develop an anaerobic energy setup working on acetylene (as proposed in Ref. [74]), then the highly energy costly process of direct production of acetylene from methane (30) becomes unnecessary. Naturally, for the most efficient use of the energy of carbon condensation, it would be reasonable to develop a cycle consisting of the direct pyrolysis of methane with the production of hydrogen and carbon vapor:

$$CH_4 \rightarrow C_{gas} + 2H_2 \ (-795 \ kJ \ mol^{-1}),$$
 (32)

with subsequent condensation of carbon into graphitized soot:

$$C_{gas} \rightarrow C_{graphite} (+720 \text{ kJ mol}^{-1}),$$
 (33)

and after separating the soot, the combustion of hydrogen (22) releases $2 \times 241.7 \approx 483$ kJ mol⁻¹, which is easily seen to yield an overall 408 kJ mol⁻¹ of environmentally-friendly energy, i.e., only half that in the process of direct combustion of methane (31).

Certainly, the technical implementation of such an energy cycle is a serious engineering problem; therefore, here, we consider only a version of the simplest layout of a setup for obtaining energy from methane without carbon dioxide formation. To implement methane pyrolysis up to atomic carbon and hydrogen, a temperature of not less than 2500 K is required. Such a temperature is nearly achieved in the combustion of hydrogen in air. Therefore, it is most natural to use a loop cycle with the combustion of the obtained hydrogen for methane pyrolysis. Figure 25 shows a schematic diagram of such an energy setup.

In the pyrolysis chamber, the inflowing methane is heated by an external hydrogen-air flame. Then, the pyrolysis products pass through a supersonic nozzle, in which they cool with the formation of soot and molecular hydrogen. The soot is separated in a separator, and the hydrogen is forwarded to an external combustion chamber, where it is mixed with air and ignited. As a result, without taking into



Figure 25. Basic diagram of environmentally-friendly energy cycle with energy production from methane without carbon dioxide emission.

account the losses and incompleteness of the pyrolysis, 408 kJ of thermal energy and 14 g of soot are obtained from a mole of methane.

Of course, in practice, it is rather difficult to implement such a process with high efficiency. The greatest problems seem to arise in relation to organizing a 100% highly endothermic process of methane pyrolysis (32) with complete dissociation of all CH_x radicals up to pure carbon vapor. As was mentioned above, the combustion temperature of the hydrogen-air mixture is about 2500 K, which is only theoretically enough for the complete pyrolysis of methane. According to the most rough estimates, even after keeping methane for several seconds at a temperature of 2500 K, up to 10% of CH_x radicals can still remain in the mixture. Moreover, technically, it is hardly realistic to heat the methane uniformly in the inner chamber up to the same temperature, which is achieved in the outer hydrogen combustion chamber. Therefore, the final elaboration of the setup design requires refined engineering calculations of kinetic, thermodynamic, heat-exchange, and gas dynamic processes in the device.

The economic reasonability of such a cycle will be determined, on the one hand, by the reduction in the energy extracted from a mole of methane with real efficiency taken into account and, on the other hand, by the cost of the carbon nanomaterial produced and the removal of penalties for the atmospheric emission of carbon dioxide.

5. Conclusion

In spite of the almost half-century history of detonation studies, this complex phenomenon still reveals new and unexplored aspects. The detonation wave of condensation, experimentally discovered and thoroughly investigated by the authors of the present review, is an absolutely new type of phenomenon, possessing a number of specific features. As pointed out in the Introduction, the usual 'physical condensation', in spite of considerable heat release, is unable to form a detonation wave. Therefore, a condition of major importance for the occurrence of a detonation wave of condensation is the process of 'chemical condensation', in which an supersaturated vapor is produced by rapid reactions of decay of the initial molecules behind a shock wave front. The subsequent heat release upon instantaneous 'explosive' condensation of this vapor is what forms the detonation wave. Certainly, such conditions can be implemented only for exothermic initial substances, as which the carbon suboxide C₃O₂ and acetylene C_2H_2 were considered.

Another important condition for the initiation and maintenance of a detonation wave of condensation is that the limiting stage ('bottleneck') of the entire process must be A V Eremin, V E Fortov

exactly the process of vapor formation via dissociation reactions exponentially accelerated with the growth of temperature. In this case, the observed heat release rate will also sharply increase with the rise in temperature, which is a necessary condition for detonation. A specific feature of the detonation wave of condensation is that, when the intensity of heat release increases so that the mixture temperature approaches the temperature of sublimation of the condensed nanoparticles, the condensation rate decreases and the wave is damped. In the review, we analyze the specific features of the kinetics of chemical condensation of carbon suboxide and acetylene, and present a simplified model of this process. The model allows describing the temperature dependences of the chemical condensation rates behind shock waves, which determine the possibility of detonation wave formation.

It is necessary to note that, in spite of all the differences between a detonation wave of condensation and classical detonation, the thermodynamics and gas dynamics of this process obey the same laws and are described well enough within the one-dimensional Zeldovich–Neumann–Döring theory, and the parameters of a steady detonation wave agree well with the Chapman–Jouguet parameters.

Finally, one more important feature of the detonation wave of condensation that offers interesting prospects for the practical application of this process is that, in contrast to the products of classical detonation of hydrocarbon fuels based on oxidation reactions, the products of such detonation do not contain carbon oxides and, therefore, this process can serve as a basis for a fundamentally new environmentallyfriendly energy cycle.

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