Chemical Condensation Wave Initiating Oxygen-Free Combustion and Detonation

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Abstract—It is well known that the propagation of traditional combustion and detonation waves was determined by the branched chain reactions discovered by Academician N.N. Semenov. This article discusses a new type of detonation waves initiated by chemical condensation processes. Chemical condensation waves arise as a result of the heat released during the explosive condensation of a highly supersaturated carbon vapor formed as a result of the dissociation of the initial carbon-containing molecules behind the front of the initiating shock wave. Unlike traditional combustion and detonation waves, the mechanism of chemical condensation does not include branched chain reactions; nevertheless, the laws of propagation of detonation waves of condensation are clearly described by the Zel’dovich—Neumann—Döring theory.

Keywords: chemical condensation, detonation, supersaturated carbon vapor, shock wave, oxygen-free combustion

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INTRODUCTION

The overwhelming part of the energy consumed by mankind is produced as a result of the combustion processes of hydrocarbon fuels, which are based on the discovered by Academician N.N. Semenov’s mechanisms of branched chain reactions leading to an avalanche-like development of ignition and the formation of deflagration and detonation waves [1]. Interest in these complex physicochemical phenomena based on the interaction of chemical, thermodynamic, and gasdynamic processes is steadily increasing both from a fundamental and from an applied point of view. In addition to an in-depth study of the multisided aspects of combustion, the search for new physical mechanisms capable of initiating energy release waves and opening up opportunities for the development of new, more environmentally friendly energy cycles is highly relevant.

From this point of view, the mechanism of the initiation of self-sustaining waves of condensation, which is known to be characterized by significant heat release, may be of particular interest. From a practical point of view, heat release during condensation can make a certain contribution to the combustion and detonation of gaseous hydrocarbons, which prevail in practice and nature, since most of these processes are accompanied by the formation of condensed carbon particles [2–4]. It is well known that the heat of condensation of carbon vapor into graphite is about 720 kJ/mol; therefore, it naturally raises the question arises on the role of this energy in the development of combustion waves and detonation of hydrocarbons. Furthermore, if this energy is so great, is it possible to generate a wave supported only by the heat released from condensation? At first glance, the answer to this question should most likely be negative: unlike ignition reactions, the condensation process does not accelerate with increasing temperature, there are no branched chain mechanisms, and the growth of condensed particles may require millions of collisions. The so-called condensation shock described by Landau [5] is known from the literature; it arises during the sharp expansion and cooling of vapor in a supersonic jet. However, as Landau noted, with all its formal resemblance to a detonation wave, this shock does not transform the flow from supersonic to subsonic, and therefore the shock wave is not supported by heat release during condensation.

Moreover, if we consider a certain volume filled with supersaturated vapor, then it is impossible to formulate conditions for the propagation of a condensation wave. Indeed, if spontaneous condensation occurs at some point of this volume, then it can only lead to a decrease in pressure, and an increase in temperature due to the release of the heat from condensation at this point will lower the degree of supersaturation and, thus, slow down the rate of condensation. Therefore, the conditions necessary for the formation and propagation of a detonation wave do not arise: an
increase in pressure and an increase in the speed of sound due to exothermic reactions (in classical detonation, during the oxidation of a combustible gas).

However, a more detailed analysis of this problem allowed the authors to formulate the conditions for the emergence of a self-sustained condensation wave. The main condition should be that the supersaturated vapor should be formed directly as a result of rapid chemical reactions of the decomposition of the initial gaseous substance in the wave front. Thus, the wave itself should initiate the formation of a highly supersaturated vapor and its subsequent immediate condensation, accompanied by a significant evolution of heat. This set of processes, in contrast to the well-known physical condensation, was called chemical condensation by the authors. Indeed, in such a situation, the process of vapor formation due to the dissociation of the initial molecules will exponentially accelerate with increasing temperature, and the subsequent exothermic recombination condensation reactions will provide a rapid and intense heat release. Of course, this initial substance must be exothermic, i.e., the integral process of its pyrolysis and the subsequent formation of the condensed phase should have a positive heat balance. The best known compound of this type is acetylene. During the pyrolysis of acetylene, graphitized soot and molecular hydrogen are formed and a significant amount of energy is released:

\[ \text{C}_2\text{H}_2 \rightarrow \text{H}_2 + \text{Graphite} + 227 \text{ kJ/mol}. \]  

The experiments were carried out behind shock waves in mixtures of carbon suboxide with argon containing 10–30% C\textsubscript{3}O\textsubscript{2} [12–15]. The temperature and pressure behind the reflected shock wave before chemical transformations (the so-called frozen parameters) were in the ranges 1400–2000 K and 4–9 bar, respectively. The actual pressure and velocity of the shock wave were measured by several piezoelectric sensors installed at distances from 0 to 300 mm from the end of the shock tube. In addition, the radiation intensity in the range \( \lambda = (633 \pm 10) \text{ nm} \) and the extinction of the laser beam, reflecting the formation of condensed particles, were recorded through various observation windows. Figure 1 shows several examples of the experimental signals. Figure 1A shows the propagation of a shock wave in a mixture of 10% C\textsubscript{3}O\textsubscript{2} + 90% Ar when the frozen temperature behind the wave is \( T_\text{f} = 1390 \text{ K} \), and the measured wave velocity is \( V_5 = 920 \text{ m/s} \). At this relatively low temperature, the chemical transformations of C\textsubscript{3}O\textsubscript{2} during measurements are insignificant [8, 9] and the shock wave propagates with constant velocity and pressure, while radiation and extinction are absent, except for a sharp schlieren signal at the moment of the passage of the shock front.

Figure 1B presents the experimental graphs observed in the same mixture, 10% C\textsubscript{3}O\textsubscript{2} + 90% Ar,
when the velocity of the reflected shockwave was \( V_5 = 1040 \) m/s, and the frozen temperature was \( T_5 = 1620 \) K. At this temperature, the process of the decomposition of \( \text{C}_3\text{O}_2 \) and the formation of carbon particles proceeds quite efficiently, and it can be seen that immediately after reaching the calculated pressure values behind the shock wave front, \( P_5 = 4.5 \) bar (dashed line), an additional increase in pressure is observed, which reaches about 6 bar. Further propagation of the shock wave is characterized by a noticeable increase in its velocity up to \( V_{\text{exp}} = 1290 \) m/s and the appearance of a sharp pressure peak immediately behind the front. These processes are accompanied by an increase in radiation peaks, which indicate a significant increase in temperature in a narrow zone behind the wave front. The bottom row of records shows an increase in extinction, reflecting the formation of condensed particles. Obviously, the condensation process also accelerates as the shock wave propagates.

In mixtures containing 20% \( \text{C}_3\text{O}_2 \) (Fig. 1C), a much faster and more intense acceleration of the shock wave from \( V_5 = 1090 \) m/s to \( V_{\text{exp}} = 1490 \) m/s, accompanied by the formation of sharp peaks of pressure and radiation, as well as abrupt condensation, was observed. It should be noted that the pressure and radiation profiles shown in Fig. 1C are quite typical for gas detonation waves [2, 16, 17]. For the subsequent series of experiments aimed at the continuous registration of the shock wave propagation process, the tube was equipped with a special additional section with two rectangular sapphire windows of 160 mm \( \times \) 5 mm, the edge of which was located at a distance of 25 mm from the end of the pipe. Time-resolved images of radiation behind the shock wave in the wavelength range of 300 to 800 nm were recorded through these windows using an ICCD camera (StreakStar II, LaVision GmbH). In addition, through the same windows at different distances from the end of the tube, the extinction of laser radiation was recorded at a wave-
length of \( \lambda = 633 \) nm, reflecting the formation of condensed particles. Figure 2 shows a diagram of the experimental setup and the main diagnostic methods.

Figure 3 shows the time base of the radiation intensity behind shock waves in mixtures of carbon suboxide with argon, initially containing 10, 20, and 30\% \( \text{C}_3\text{O}_2 \). The frozen temperatures behind the front of the reflected shock wave are in all cases so low that the radiation of the mixture before the heat release could not be detected. In the case of a 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 radiation overtakes the shock front in the region of the middle of the window and accelerates the shock wave from \( V_s = 1050 \) to \( 1300 \) m/s. In a mixture containing 20\% \( \text{C}_3\text{O}_2 \), despite the lower frozen temperature, the condensation wave reaches the shock front much earlier. Immediately after this, a bright emission peak is formed at the front, and then a stable shock wave velocity of \( \sim 1500 \) m/s is observed (at the initial value \( V_s = 1050 \) m/s).

In the mixture with 30\% \( \text{C}_3\text{O}_2 \), the most surprising behavior of the shock wave is observed: at first it accelerates from \( V_s = 1100 \) to \( 1600 \) m/s and then decelerates to \( 1300 \) m/s. The reason for this nonmonotonic behavior of the detonation condensation wave with the increasing intensity of the initiating shock wave lies in the fundamental difference between the condensation kinetics and the kinetics of combustion processes. With an increase in temperature and as it approaches to the temperatures of the phase transition (sublimation) of the forming nanoparticles, the effective rate of their condensation inevitably decreases and at certain temperatures becomes lower than the rate of their decay (disintegration) [10, 18].

ANALYSIS OF THE OBTAINED RESULTS

The efficiency of the contribution of the condensation energy to the dynamics of the initiating shock wave strongly depends on the real time of the growth of the particles to their final size. This time can be qualitatively estimated from the extinction profiles shown in Fig. 1c (B, C). It can be seen that, with an increase in the shock wave intensity (and an increase in temperature), this time decreases from 80 to 10 \( \mu \)s. It is important to note again that the reason for the apparent acceleration of condensation with increasing temperature is that the limiting stage that determines the rate of the entire process is the dissociation reaction of carbon suboxide \( \text{C}_3\text{O}_2 \to \text{CO} + \text{C}_2\text{O} \) with a constant
Fig. 3. Time scale of the radiation intensity and cross section at its maximum values behind the shock front in mixtures initially containing 10 (a), 20 (b) and 30% (c) C$_2$O$_2$ in Ar. The initial pressure behind the front of the reflected shock wave in all experiments was (6 ± 1) atm; $T_5 = 1650$ (a), 1530 (b), and 1490 K (c).

rate $k_d = 2 \times 10^{15}\exp(-10720T)$ cm$^3$ mole$^{-1}$ s$^{-1}$ [7]; all the other reactions proceed faster. It was shown in the experiments [19] that up to temperatures $T \geq 2200$ K, the effective particle growth rate constant practically coincides with $k_d$. However, this behavior of the process is realized until the reverse reactions of the decomposition of clusters and nanoparticles come into play due to an increase in temperature. It was shown in [9, 10] that as the temperature behind the shock wave increases to 2800–3000 K, the rate of particle formation slows down. At $T = 3000$ K, the total time of particle growth is more than 100 µs, and at $T = 3400$ K the rate of the decay (evaporation) of the particles is higher than the rate of their formation [10]. 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 the process should become self-decaying upon excessive overheating.

This reasoning is clearly illustrated in Fig. 4 comparing the observed parameters of the shock wave with the behavior of the Hugoniot adiabats [20, 21] for the initial mixtures (curves I) and for mixtures after condensation (curves II). The straight lines 2–5 correspond to the calculated velocity of the reflected shock wave. Points 6 and rays 2–6 show the experimentally measured pressure maximums and the velocity of the accelerated wave front. Points $P_{exp}$ show the steady-state pressure values, and points $C$–$J$ demonstrate the Chapman–Jouguet detonation parameters calculated in the one-dimensional approximation [21].
It can be seen that in a mixture of 10% C₂O₂ + Ar (Fig. 4a), ray 2–6 crosses adiabat II at markedly lower pressures than $P_{\text{exp}}$, and the measured wave velocity is slightly higher than the Chapman–Jouguet velocity (tangential to curve II from point 2). This behavior of the wave can be caused by insufficient heat release, in which case the wave propagation continues to be supported by the pressure of the gas compressed at the end of the tube behind its front. This flow mode is commonly referred to as over-compressed detonation.

In a mixture of 20% C₂O₂ + Ar (Fig. 4b) there is a very good agreement between the measured and calculated values of the pressure and wave velocity. Under these conditions, the calculated temperature behind the detonation front is 2460 K, which, according to [10, 22–24], corresponds to almost the maximum condensation rate. This fact is clearly demonstrated by the extinction profile in Fig. 1c.

In a richer mixture of 30% C₂O₂ + Ar (Fig. 4c), the measured values of pressure and wave velocity lie below the calculated values of the detonation parameters. This can be explained by the excessive heat release, leading to incomplete condensation when the temperature rises above 2800 K. At these temperatures, particle decay processes begin to play a role, slowing the effective condensation rate. As a result, the condensation energy cannot be completely transferred to the wave dynamics, and the so-called damped, under-compressed detonation mode is observed.

Thus, the studies have shown quite convincingly that there are conditions under which a detonation wave is formed and maintained exclusively due to the
Fig. 3. (Contd.)

Fig. 4. Behavior of Hugoniot adiabats for the initial mixtures (curves I) and for mixtures after condensation (curves II): (a) mixture of 10% C_3O_2 + Ar, \( T_{C-J} = 2050 \) K; (b) mixture of 20% C_3O_2 + Ar, \( T_{C-J} = 2460 \) K; (c) mixture of 30% C_3O_2 + Ar, \( T_{C-J} = 2830 \) K.
condensation energy of carbon nanoparticles. Based on the results of these studies, it can be argued quite definitely that the mechanism for the occurrence of deflagration and detonation waves, which are repeatedly observed in acetylene, is also based on the phenomenon of chemical condensation.

CONCLUSIONS

In the studies carried out, a new physical phenomenon was observed: the formation of a detonation wave, supported exclusively by the condensation energy of a highly supersaturated carbon vapor formed during the dissociation of carbon-containing molecules directly behind the front of the initiating shock wave. This type of condensation has been called chemical condensation. It is important to note here that, despite the fundamental difference between the kinetics of chemical condensation and the traditional kinetic mechanisms of ignition and detonation, i.e., the absence of branched chain reactions, the thermodynamics and gas dynamics of the detonation wave of chemical condensation completely obey the same laws and are fairly well described in the one-dimensional Zeldovich—Neumann—Döring theory, and the parameters of the steady-state detonation wave coincide well with the Chapman—Jouguet parameters.

Another important feature of the chemical condensation wave, which opens up interesting prospects for the practical use of this process, is that, in contrast to the classical combustion and detonation of hydrocarbon fuels based on oxidation reactions, this process is completely anoxic and its products do not contain carbon oxides. Thus, it can be used as the base for the development of a fundamentally new and environmentally friendly energy cycle.

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