Detonation Wave Driven by Energy of Carbon Condensation

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Pyrolysis, combustion and detonation of hydrocarbons are almost always accompanied by the formation of condensed carbon nanoparticles, which usually are called “soot”. In most cases, at least when using processes of combustion and detonation for energy production, the major task is to decrease a soot emission. However, in some other applications, let say, when using combustion for lighting and, especially in all technological processes on production of any carbon nanoparticles, from black carbon to fullerenes, nanotubes and nano-diamonds, not energy yield, but just formation of the condensed carbon – is the main product of proceeding reactions.

Nevertheless, there is one circumstance which is almost always overlooked – a process of formation of the condensed particles from the gas phase, or in other words, condensation, is an exothermic reaction, which is accompanied by a considerable heat release. In particular, it is well known that the heat of condensation of carbon vapor to graphite is about 720 kJ/mol. Therefore quite naturally is to raise a question – what is a role of this energy at detonation of hydrocarbons? And, moreover, if this energy is so considerable, is it possible to generate a detonation wave, which is driven only by the heat release of condensation?

At first sight, the answer is rather negative – unlike the ignition reactions, the process of condensation does not accelerated with the temperature rise, the chain branching mechanisms are not present and the times of particles growth are likely too long.

On the other hand, many years ago, at the end of nineteenth century Berthelot and Le Chatelier for the first time observed the process of detonation at self-decomposition of acetylene [1]. It is well known that the products of this process are molecular hydrogen and condensed carbon – soot, and no exothermic oxidation reactions take place. Since that time this process, certainly, was investigated by numbers of authors. However to determine quantitatively a contribution of energy of condensation to formation of a detonation wave in this process was quite difficult because of existence of a large number of complex intermediate reactions of growth of the polyatomic hydrocarbons preceding the formation of condensed carbon particles. Nevertheless, high heat of condensation of carbon vapor allows raising quite natural question of an essential role of this energy in the formation of a detonation wave at acetylene self-decomposition.

*Starting this study we have managed to formulate the conditions of emergence of a detonation wave of condensation. The main condition is that the carbon vapor has to be formed as a result of fast chemical reactions of decomposition of the carbon-bearing species behind the front of a shock wave. Thus, shock wave has to initiate the processes of formation of strongly supersaturated vapor and its subsequent immediate condensation, being accompanied by an essential heat release. Such set of processes unlike well known "physical condensation" can be called "***chemical condensation***". Really, in such a situation the process of vapor formation, as well as ignition, will exponentially accelerate with temperature rise, and the subsequent exothermic recombinational reactions of condensation will provide a fast and intensive heat release.

Such statement of the problem was formed based on our recent results, where the phenomenon of a considerable heating up of the reacting mixture, caused by the condensation of carbon vapor, formed at shock wave pyrolysis of carbon suboxide C_3O_2 was observed [2].

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Carbon suboxide — is quite unstable volatile compound and when heating to 1400–1600 K its molecules quickly decompose, forming carbon atom and two molecules CO. The important feature of this process is that a limiting stage ("a bottle-neck") for growth of the condensed particles is the reaction of formation of the carbon vapor, the rate of which exponentially increases with temperature rise. At the temperatures of 1800-2500 K and pressure of 3-30 bar the stage of cluster growth to the size of 10^3-10^4 atoms, which is accompanied by an intensive heat release, lasts about 1-10 μs. Another important specifics of the process of carbon suboxide decomposition and the subsequent condensation of carbon — is the total absence of secondary gaseous reactions (at C_3O_2 dissociation there is only a carbon vapor and CO molecules, which are chemically stable up to T ~ 4000 K, remain in the mixture). This fact gives an opportunity to carry out the simple analysis of interrelation of growth of the clusters and a heat release behind shock waves of various intensity.

For the observation of the development of detonation wave the special section of shock tube was built. This section was equipped with 2 rectangular sapphire windows 160 mm long installed at distance of 25 mm from the end plate. Through these windows the time and space resolved record of radiation behind a shock wave by means of Streak-Star Camera (LaVision) has been carried out. Besides that in this section several calibrated pressure piezo-sensors also were built in (Fig.1).

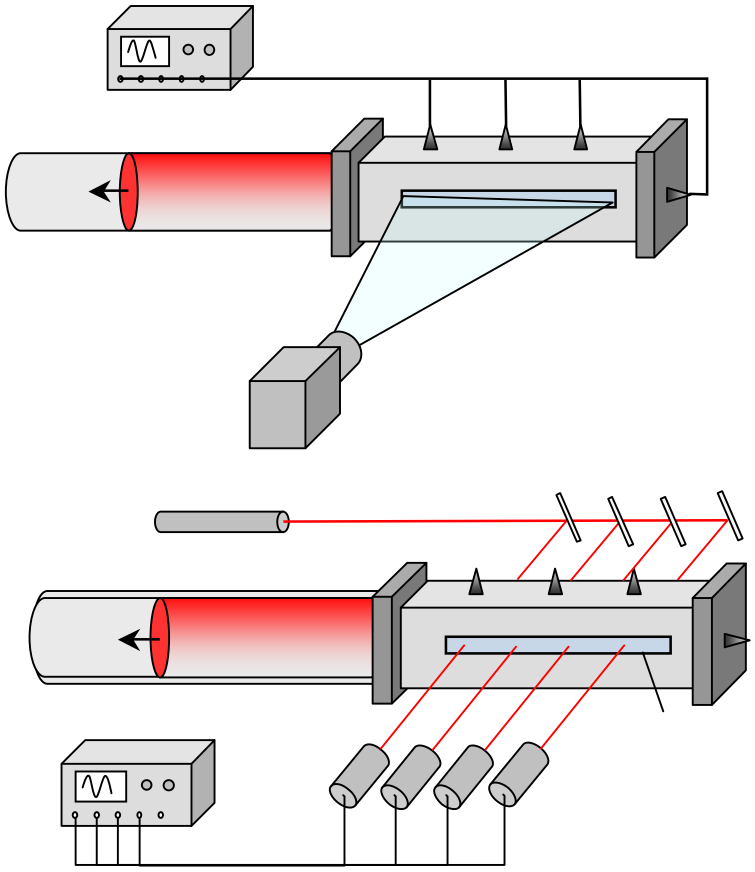
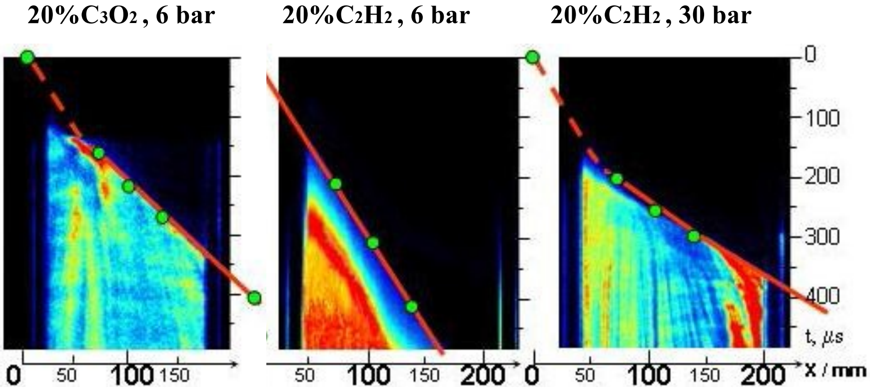


Fig. 1. Diagram of a shock tube and scheme of a multichannel diagnostics of the formation of a detonation behind the reflected shock wave (RS) with the use of pressure transducers (G1–G4), a time scan of radiation with the use of rectangular sapphire windows (W) and an ICCD camera, and of a measurement of the laser extinction or the self-radiation of the flow with the use of a continuous helium–neon laser, a system of mirrors (M), and photomultiplier tubes (P1–P4).

In Fig.2 the propagation of shock wave in the mixtures, containing 20% C_3O_2, or 20% C_2H_2 at various pressures are compared. A vertical scale shows time, horizontal – shows distance. Fig.2a represents process of formation of a detonation wave in C_3O_2. One can see that in the beginning of observation zone the condensation wave (characterized by heating and, accordingly, radiation rise) catches up the front of a shock wave marked by a red line, strengthens and accelerates a shock wave and forms detonation-like structure with the radiation and pressure peaks at the front. However, unlike C_3O_2, in acetylene at the same initial pressure 6 bar (see Fig.2b) the wave of condensation, which is clearly seen due to intensive heating of a mixture, is separated from front of a shock wave by a wide zone (about 50 mm) invariable within observation region. In other words, in these conditions the wave of condensation does not influence on an initiating shock wave which continues to move with a constant velocity. At pressure increase in the same mixture up to 30 bar (Fig.2c) the picture essentially changes – the condensation wave quickly catches up a shock wave, accelerates it and forms the detonation-like structure rather similar observed in C_3O_2.



a **b** **c**

Fig. 2. ICCD images of shock wave propagation in various conditions. Green points and red lines show the trajectories of shock wave front measured by the pressure gauges.

To check the correspondence of observed regimes to parameters of detonation waves in investigated mixtures the evaluations on the basis of the one-dimensional theory of a detonation have been carried out. In the following Fig.3 the comparison of measured wave velocity and pressure behind it with behavior of adiabatic Hugoniot curves for initial mixtures (curves I), and for mixtures after condensation (curves II) are shown. Straight lines 2 – 5 represent the initial velocity of the reflected shock wave. Points 6 and rays 2 – 6 represent experimentally measured maximum peaks of pressure and velocity of front of a wave after its acceleration. Points P_{exp} show the established values of pressure and point C-J show parameters of Chapman-Jouguet detonation calculated in one-dimensional approach. It is well seen that in both mixtures the investigated regimes are in a good coincidence with the calculated Chapman-Jouguet parameters.

From this consideration it follows that though in both mixtures actually the detonation waves are formed, the threshold pressure of detonation formation in acetylene appears essentially higher, than in C_3O_2, despite larger heat effect of reaction:

$$C_2H_2 \rightarrow 2C(\text{graphite}) + H_2 \, (+\,277 \text{ kJ/mole}),$$

than reaction:

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$$C_3O_2 \rightarrow C(\text{graphite}) + 2CO \, (+\,142 \text{ kJ/mole}).$$

Therefore it becomes clear that a principal reason of a difference in a process of detonation wave formation in C_2H_2 from C_3O_2 is the different rates of a heat release and for the analysis of this process it is necessary to investigate the peculiarity of kinetics of carbon condensation during pyrolysis of these two substances.

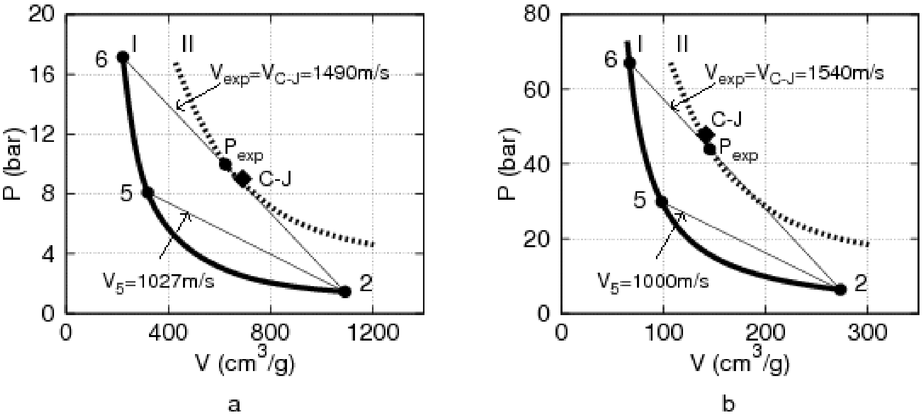

Fig.3. The behavior of Hugoniot adiabatic curves and observed detonation regimes in C_3O_2 and C_2H_2.Curves I are the adiabatic curves for the initial mixtures and curves II - for the mixtures after condensation . (a) - mixture 20%C_3O_2+Ar, T_{C-J} = 2460 K; (b) – mixture 20%C_2H_2+Ar, T_{C-J} = 2517 K. Points 2 are initial states of the mixtures before shock wave, points 5 are the "frozen" parameters behind shock wave, points 6 are the peak pressures behind the accelerated wave, P_{exp} are established pressures behind the detonation wave, points C-J are Chapman-Jouguet parameters.

Really, if at pyrolysis of C_3O_2 atoms and clusters of carbon are the primary products of dissociation, which immediately start being condensed in nanoparticles, in contrast to that, products of dissociation of C_2H_2 are the hydrocarbon radicals, which start being polymerized, but do not form the carbon particles. During the further reactions the complex hydrocarbon radicals either polyacetylenes, or polyaromatics kind are formed. And these reactions are not still accompanied by noticeable heat release. The further stage of process, characterizing by formation of carbon particles, is accompanied by the essential heat release and the following rise of current temperature of the mixture and collapse of the whole process with the formation of a detonation wave.

Conclusions:

- A new physical phenomenon – detonation wave driven by energy of carbon condensation has been observed.
- The interconnection of kinetics of condensation and the heat release processes has been investigated
- The most significant heat release proceeds during the last stage of the process – the formation of condensed particles.

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References

[1] Berthelot M and Le Chatelier HL. (1899). Sur la vitesse de detonation da l' acetylene, Comptes Rendus, 129:2:427–434.

[2] Emelianov AV, Eremin AV, Makeich AA, Jander H, Wagner HGg, Starke R, and Schulz Ch. (2007) Heat release of carbon particle formation from hydrogen-free precursors behind shock waves, Proc. Combust. Inst. 31:649–656.