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Detonation wave driven by condensation of supersaturated carbon vapor

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An experimental observation of a detonation wave driven by the energy of condensation of supersaturated carbon vapor is reported. The carbon vapor was formed by the thermal decay of unstable carbon suboxide C_3O_2 behind shock waves in mixtures containing 10–30% C_3O_2 in Ar. In the mixture 10% C_3O_2+Ar the insufficient heat release resulted in a regime of overdriven detonation. In the mixture 20% C_3O_2+Ar measured values of the pressure and wave velocity coincident with calculated Chapman-Jouguet parameters were attained. In the richest mixture 30% C_3O_2+Ar an excess heat release caused the slowing down of the condensation rate and the regime of underdriven detonation was observed.

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Lately there has been a renewed interest in detonation problems. This phenomenon, studied already for more than a century [1], still has many unanswered questions [2,3]. In addition to the classical detonation, initiated by exothermic reactions in fuels and explosives, the formation of "light-detonation waves," generated by the impact of laser radiation, was recently predicted [4] and observed [5]. Among the applications (besides the constantly growing importance of safety) is the extremely active research area of pulse detonation engines, which could be a more effective energy converter than traditional combustion engines [3]. Finally, one more rather promising application of a detonation is the synthesis of nanodiamonds [6] and other types of nanoparticles [7]. Therefore a search for new physical mechanisms capable of initiating a detonation is a quite topical problem.

One such mechanism is the process of condensation, accompanied by the essential heat release. From the practical point of view, this mechanism can contribute to detonation of gaseous hydrocarbons, predominant in practice and in nature, since most of these processes are accompanied by the formation of condensed carbon particles [1,6]. Very recently a study of the process of carbon cluster formation in detonation waves in various gas mixtures was published [7]; however, the quantitative contribution of condensation energy to a detonation wave has not been investigated hitherto to our knowledge. On the other hand, the discovery of the conditions for the generation of a detonation wave driven only by the heat release of condensation is intriguing.

Recently [8], the phenomenon of considerable heating of a reacting mixture, caused by the condensation of carbon vapor formed during the shock wave pyrolysis of carbon suboxide C_3O_2, was observed. Carbon suboxide is a rather unstable volatile compound and under heating up to 1400–1600 K its molecules decompose to a carbon atom and two CO molecules. The complete transformation

$$C_3O_2 \rightarrow CO + \textit{carbon nanoparticles}$$

in mixtures containing only 3% C_3O_2 in Ar resulted in a temperature rise of 300 K [8]. Estimations have shown that the observed heat release (~120 kJ/mol) is rather high and comparable with the combustion of hydrogen-air mixtures (~140 kJ/mol). An important peculiarity of this process is that the limiting pathway for condensed particle growth is the reaction of carbon vapor formation, exponentially accelerating with temperature [8,9]. At temperatures between 1800 and 2500 K and pressures between 3 and 30 bar, a stage of cluster growth up to the sizes 10^3-10^4 atoms, which is accompanied by active heat release, lasts for approximately $1-10$ μs. Therefore one can assume that at appropriate conditions the process of energy liberation can proceed in a heat explosion regime and form a self-sustaining detonation wave.

Another important property of the process of C_3O_2 decomposition and consequent carbon condensation is the total absence of secondary gaseous reactions. (Only CO remains in the system, which is chemically stable for $T<4000$ K.) This fact presents the opportunity to perform a reliable analysis of the relationship between cluster growth and heat release behind shock waves of various intensities.

This Rapid Communication presents an experimental observation of the influence of supersaturated carbon vapor condensation (formed behind shock waves in the mixtures C_3O_2+Ar) on the process of shock wave propagation and formation of a detonation wave of condensation.

Experiments were performed behind reflected shock waves in a shock tube of 70 mm inner diameter in mixtures initially containing 10–30 % C_3O_2 in Ar. The temperature and pressure behind the reflected shock wave before chemical transformations ("frozen" parameters) were in the range 1400−2000 K and 4−9 bar. The actual pressure and shock wave velocity were measured by several piezogauges installed at various distances 0−300 mm from the end plate of the shock tube. In addition, the radiation intensity at $\lambda=633\pm10$ nm and laser light attenuation (or extinction), depicting the condensed particle formation, were recorded at various measurement windows. Figure 1 shows several sample experimental traces. Figure 1(A) shows the propagation of a shock wave in the mixture 10% C_3O_2+90% Ar, when the frozen temperature behind the wave is $T_5=1390$ K. At this relatively low temperature the chemical transformation of C_3O_2 during the residence time is negligible [9] and the shock wave demonstrates a steady velocity

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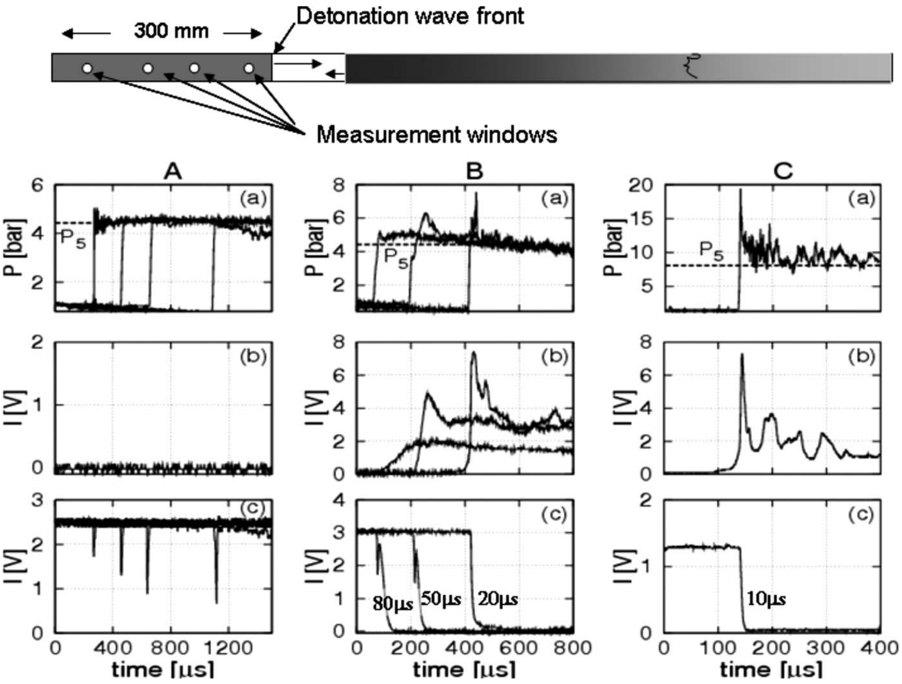

FIG. 1. Schematic of shock tube and measurement windows and the time profiles of pressure (a), radiation at 633 nm (b) and laser light attenuation (extinction) (c), measured behind shock waves in the mixtures C_3O_2+Ar at various distances (70, 140, and 295 mm) from the end plate of shock tube. Mixtures and frozen temperatures T_5 behind the wave near end plate: (A) the 10% C_3O_2+Ar, T_5=1390 K; (B) 10% C_3O_2+Ar, T_5=1620 K; (C) 20% C_3O_2+Ar, T_5=1440 K. Embedded values in plots (Bc) and (Cc) show the characteristic time of extinction increase.

(V_5=920 m/s) and pressure. No radiation or extinction (except for the sharp schlieren signal at the moment of shock front passage) is observed. Figure 1(B) represents experimental plots, observed in the same mixture 10% C_3O_2 +90% Ar, when the calculated velocity of the reflected shock wave was V_5=1040 m/s and the frozen temperature was higher (T_5=1620 K). At this temperature the process of C_3O_2 decomposition and carbon particle formation proceeds quite effectively, and one can see that immediately after achievement of the calculated values of pressure behind the shock wave front (P_5=4.5 bar, dashed line) an additional pressure rise up to about 6 bar is observed. Further propagation of the shock wave is characterized by the noticeable increase of its velocity up to V_{expt}=1290 m/s and appearance of a sharp pressure peak just behind the front. These processes are accompanied by the rise of radiation peaks testifying to a temperature increase in the narrow zone behind the wave front. The lower row of records demonstrates the rise of extinction, reflecting the formation of condensed particles. Obviously the condensation process is also accelerating with the propagation of the wave.

In the mixtures containing 20% C_3O_2 [Fig. 1(C)] a much faster and more intensive acceleration of the shock wave from V_5=1090 m/s up to V_{expt}=1490 m/s, accompanied by the formation of sharp peaks of pressure and radiation as well as stepwise condensation, has been observed. The profiles of pressure and radiation, shown in Fig. 1(C), are quite typical for gaseous detonation waves [1,2].

In Fig. 2 the temperature dependence of the shock wave velocity measured in the mixture 10% C_3O_2+Ar at 195 mm from the end plate of the shock tube is compared with the computed values for frozen conditions. The acceleration of the shock wave starts at temperatures above 1500 K, corresponding to onset of the thermal decomposition of C_3O_2 [9]. At temperatures above 2500 K the velocity difference comes to a maximum, indicating the entire input of the condensation energy to the dynamics of the shock wave. Note that the control experiments in nonreacting mixtures showed a very good agreement between the calculated and measured velocities of the reflected shock wave ($\Delta V/V \leqslant 0.01$).

Condensed carbon nanoparticles formed behind the wave were analyzed using x-ray spectroscopy and electron microscopy. Particles consist of pure carbon, have the structure of amorphous graphite, and look like spheres with an average size ~15–30 nm (see Fig. 3).

To analyze the observed phenomena, recent data on the heat release of carbon particle formation during the thermal

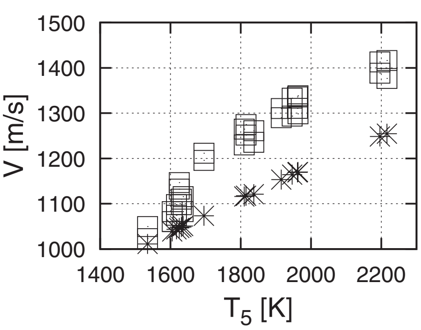

FIG. 2. Comparison of shock wave velocity V_{expt} (□) measured at 195 mm from the tube end with the values V_5 (*) calculated for frozen conditions. Mixture: 10% C_3O_2+Ar.

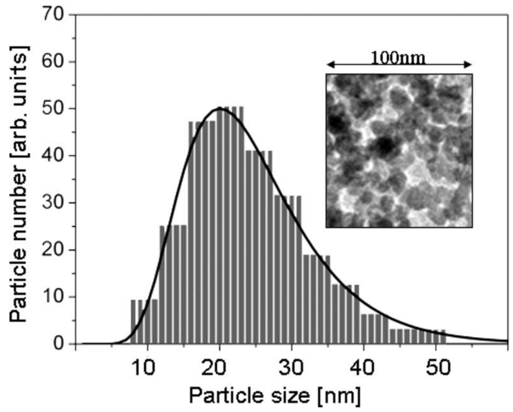

FIG. 3. Size distribution of carbon nanoparticles formed behind the shock wave in the mixture 20% C_3O_2+Ar.

decomposition of C_3O_2 behind shock waves [8] were used. Numerical calculations of the kinetics of C_3O_2 dissociation and the subsequent condensation of carbon vapor, accounting for the energy balance of each reaction, were performed using the kinetic scheme proposed in [10]. The total heat Q released from the reaction

$$C_3O_2 \rightarrow 2CO + C_N/N$$

is calculated from

$$Q = \Delta H_f(C_3O_2) - \Delta H_f(CO) - \Delta H_f(C_N),$$

where ΔH_f are the enthalpies of formation of the mixture components. In the above reaction, N is the number of carbon atoms in a particle.

The main uncertainty in the calculations was caused by the lack of reliable data on the equations of state and enthalpies of formation of carbon nanoparticles of various sizes. In Fig. 4 the approximation $Q=f(N)$, based on data taken from Refs. [8,11,12], is presented. According to the accepted values, the dissociation energy of C_3O_2 ($\sim$573 kJ/mol) is already compensated for at the cluster size $N \approx 20$ atoms, and later the process becomes exothermic. One can see from Fig. 4 that at final particle size 20 nm (which corresponds at particle density 1.86 g/cm^{-3} [13] to $N \approx 10^6$ atoms) the heat of reaction approaches $\sim$120 kJ/mol.

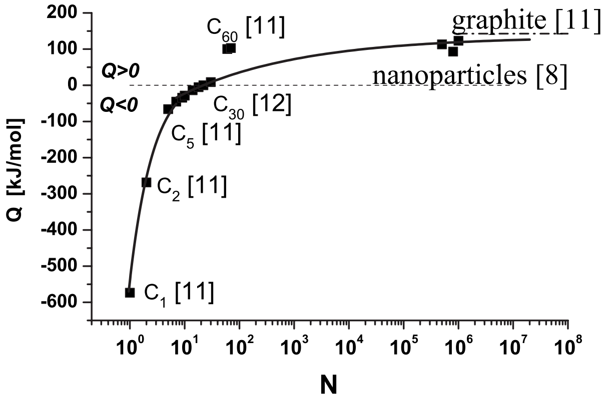

FIG. 4. Total heat balance of the process $C_3O_2 \rightarrow 2CO + (1/N) C_N$ as a function of the final particle size N.

The efficiency of the contribution of the energy of condensation to the shock wave dynamics strongly depends on the real time growth of the particles up to their final size. Qualitatively this time can be estimated from the extinction profiles shown in Figs. 1(Bc) and 1(Cc). One can see that with the amplification of the shock wave (and the associated temperature rise), this time decreases from 80 to 10 μs. It was already mentioned above that the reason for the apparent acceleration of condensation with the temperature rise is that the rate-determining step of the whole process is the decomposition reaction $C_3O_2 \rightarrow CO + C_2O$ which has a rate constant $k_d \approx 2 \times 10^{15} \exp(-225 \text{ kJ/mol}/RT)$ cm^3 mol^{-1} s^{-1} [9]. All other reactions proceed faster. In experiments [8] it was shown that the effective rate constant of particle growth practically coincides with k_d. However, this behavior of the process is correct until the reversal reactions of nanoparticle decay come into play.

Toward temperatures higher than 2500 K, the particle formation rate becomes slower [14]. At T=3000 K the total particle rise time is more than 100 μs and at T=3400 K the rate of particle decay (evaporation) is already higher than the formation rate [14]. Therefore it is obvious that, in contrast to classical detonation caused by combustion processes, the phenomenon discussed herein must have an extreme dependence on integral heat release and the process will become self-destructive at excessive overheating.

This reasoning is clearly illustrated in Figs. 5(a)–5(c) by the comparison of the observed shock wave parameters with the behavior of Hugoniot adiabatic curves [1,2] for the initial mixtures (curves I) and for the 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 experimentally measured pressure maxima and velocity of the accelerated wave front. Points P_{expt} show the steady pressure values and the points C-J demonstrate the Chapman-Jouguet parameters of detonation, calculated using a one-dimensional approximation [1,2].

One can see that in the mixture 10% C_3O_2+Ar [Fig. 5(a)] ray 2-6 intersects adiabat II at the pressure coincident with the value P_{expt}, which is larger than $P_{\text{C-J}}$, and the measured velocity of the wave is a bit higher than the Chapman-Jouguet velocity (tangent to curve II from point 2). This behavior of the wave can be caused by insufficient heat release resulting in the wave being supported by the pressure behind it. Such a flow regime is usually called overdriven detonation.

In the mixture 20% C_3O_2+Ar [Fig. 5(b)] very good agreement between measured and calculated values of pressure and wave velocity is observed. At these conditions the calculated temperature behind the detonation front is 2460 K, which, according to [14], corresponds to nearly the maximum condensation rate. This fact is clearly demonstrated by the extinction profile in Fig. 1(Cc).

In richer mixture 30% C_3O_2+Ar [Fig. 5(c)] the measured values of pressure and wave velocity lie below the calculated parameters of detonation. This fact could be explained by the excess heat release resulting in incomplete condensation at a

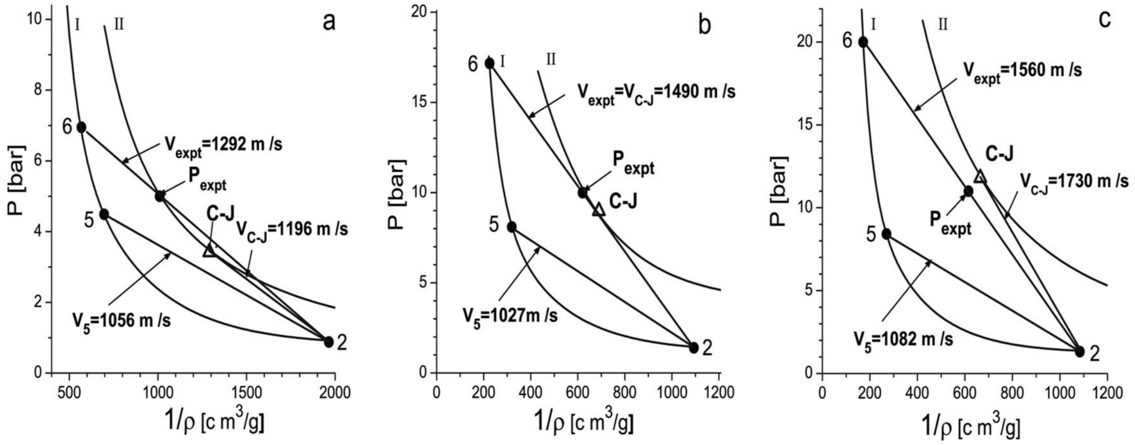

FIG. 5. Behavior of Hugoniot adiabatic curves for the initial mixtures (curves I) and for the mixtures after condensation (curves II). (a) mixture 10% C_3O_2+Ar, $T_{\text{C-J}}$=2050 K; (b) mixture 20% C_3O_2+Ar, $T_{\text{C-J}}$=2460 K; (c) mixture 30% C_3O_2+Ar, $T_{\text{C-J}}$=2830 K.

temperature rise above 2800 K. At these temperatures the reversal processes of particle decay, which slow down the effective condensation rate, begin to play a role. Owing to that, the energy of condensation cannot be completely transmitted to the wave dynamics and the so-called regime of damping, an underdriven detonation, is observed.

In summary, this paper presents the observation of the phenomenon of formation of a detonation wave that is driven by the condensation of a supersaturated vapor. The important practical application of this issue is the new understanding of the role of condensation processes in the detonation of gaseous fuels that yield condensed products.

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