Detonation wave initiated by explosive condensation of supersaturated carbon vapor

A. Emelianov[1], A. Eremin[1], V. Fortov[1], A. Makeich[1], H. Jander[2], H. Gg. Wagner[2], J. Deppe[3]

[1] Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia

[2]Institut für Physikalische Chemie, Göttingen Universität, Germany

[3]LaVision, Göttingen, Germany

1 Introduction

It is known, that the detonation of most gaseous hydrocarbon fuels is accompanied by the formation of condensed carbon particles and the process of condensation, just as the oxidation reactions, is characterized by the essential heat release. In the recent paper [1] the process of carbon cluster formation behind detonation waves in acetylene-air and acetylene-oxygen mixtures has been studied, however the quantitative input of condensation energy to the detonation wave was not discussed in details. On the other hand the rightful question is the possibility of realization of conditions for the generation of a detonation wave driven only by the heat release of condensation.

Recently [2], the phenomenon of considerable heating of reacting mixture, caused by the condensation of carbon vapor formed during the shock wave pyrolysis of carbon suboxide C_3O_2, was for the first time observed. Carbon suboxide is rather unstable volatile compound and under heating up to 1400 – 1600 K its molecules decompose to carbon atom and two CO molecules. A complete transformation:

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

in the mixtures containing only 3% C_3O_2 in Ar resulted in the additional temperature rise up to 300 K [2]. An important peculiarity of this process is that a bottleneck of condensed particle growth is the reaction of carbon vapor formation, exponentially accelerating with the temperature rise [3]. At the temperatures 1800 – 2500 K and pressures 3 – 30 bar a stage of cluster growth up to the sizes 10^3 – 10^4 atoms, which is accompanied by the active heat release, lasts at about 1 – 10 μs [4]. Therefore one can assume that at appropriate conditions the process of condensation and energy liberation can proceed in a heat explosion regime and form a detonation wave.

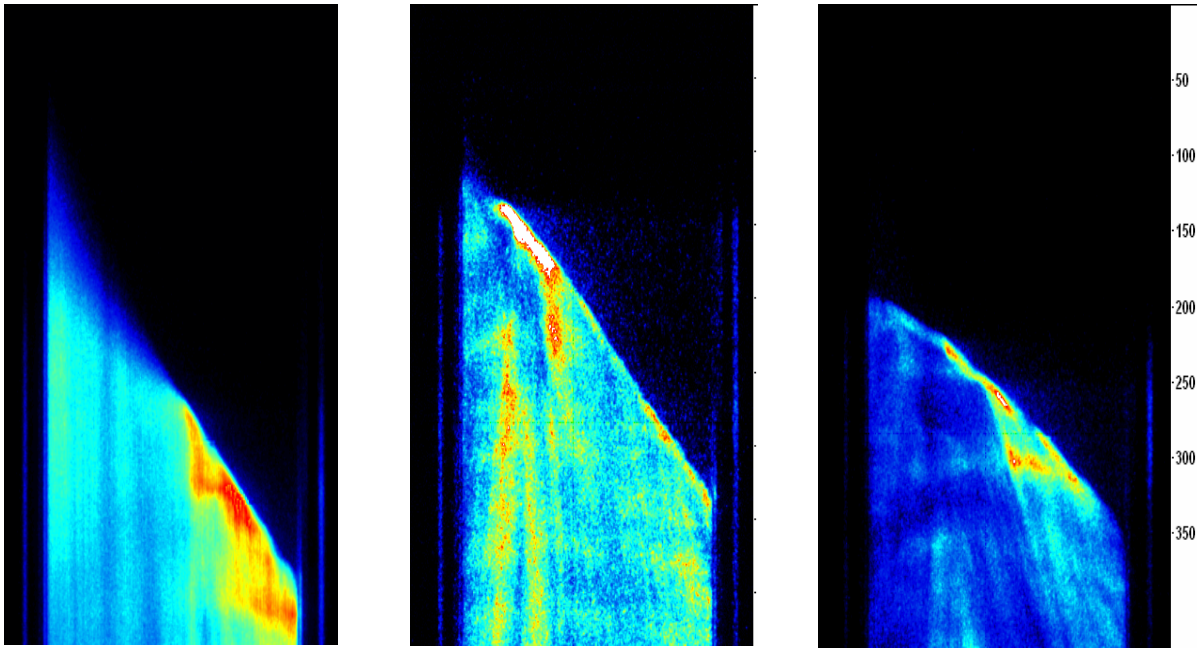
Another important property of the process of C_3O_2 decomposition and consequent carbon condensation is the total absence of secondary gaseous reactions (in the system remains only CO, which is chemically stable at T < 4000K). This fact presents the opportunity to perform a plain analysis of interconnection of cluster growth and heat release behind shock waves of various intensities. Based on this analysis one can estimate the threshold parameters of detonation wave

Correspondence to: Eremin@ihed.ras.ru

formation. However for reliable confirmation of such a phenomenon experimental measurements of a change of shock wave parameters at different concentrations of C_3O_2 have been necessary.
This paper presents the first experimental observation of an 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 principally new phenomenon – detonation wave of condensation.

2 Experimental

The experiments were carried out in a high pressure shock tube of 70 mm inner diameter and 4.5 m long driven section. The propagation of reflected shock waves in the mixtures, initially consisting of 10 – 30 % C_3O_2 + Ar have been studied. Temperature and pressure behind reflected shock wave before chemical transformations ("frozen" parameters) were in the range 1350 – 1750 K and 4 – 9 bar. The actual pressure and shock wave velocity were measured by several piezo-gauges installed at the various distances 0 – 300 mm from the end plate of shock tube. For the observation of shock wave behavior the shock tube was equipped by two rectangular sapphire windows 160 mm x 5 mm installed on the distance 25 mm from the end plate. Through these windows the time resolved images of radiation behind shock wave in the range 300 – 800 nm were recorded using an ICCD camera (StreakStar II, LaVision GmbH). Besides that the laser light attenuation (or extinction) at λ = 633 ±10 nm, depicting the condensed particle formation, was registered through the same windows at the different distances from the end plate.



10% C_3O_2 + Ar
T_5(frozen) = 1650 K
V_5(frozen) = 1050m/s
V_{max} = 1300 m/s

20% C_3O_2 + Ar
T_5(frozen) = 1530 K
V_{max} = 1500 m/s

30% C_3O_2 + Ar
T_5(frozen) = 1490 K
V_{max} = 1600 m/s

Fig.1. Time and distance resolved records of radiation intensity behind reflected shock waves in the mixtures initially contained 10, 20 and 30% C_3O_2 in Ar. Time – vertical scale, distance – horizontal scale. Right upper corner corresponds to the moment of shock wave reflection.

In Fig.1 the time-scanning of radiation behind the shock waves in the mixtures, initially contained 10, 20 and 30% C_3O_2 in Ar are shown. The "frozen" temperatures in all cases are so low that radiation of the mixture before the heat release processes could not be seen. In the first case of 10% C_3O_2 the heat release condensation wave overtakes the shock wave front somewhere at the middle of the window and speeds it up to the 1300 m/s against the initial value V_5 = 1050m/s. In the mixture 20% C_3O_2, despite of the less "frozen" temperature, the condensation wave overtakes shock front much earlier and supports the stable shock wave velocity ~ 1500 m/s (against initial V_5 = 1090m/s). And in the mixture 30% C_3O_2 shock front first accelerates up to 1600 m/s and then slows down to 1300 m/s. Similar behavior show the records of the pressure and extinction. In Fig.2 the comparison of pressure, radiation and extinction time-profiles measured at the various distances from the end of shock tube in the mixtures 10% C_3O_2 at two different intensities of shock wave is shown. Case A, corresponding to the non-reactive conditions (T_5 = 1390 K) demonstrates the stable pressure (equal to P_5) shock wave velocity and no signals of radiation and extinction. At higher T_5 = 1620 K the propagation of shock wave is accompanied by the rise of pressure and radiation peaks and increasing rate of extinction rise reflecting the immediate formation of condensed particles.

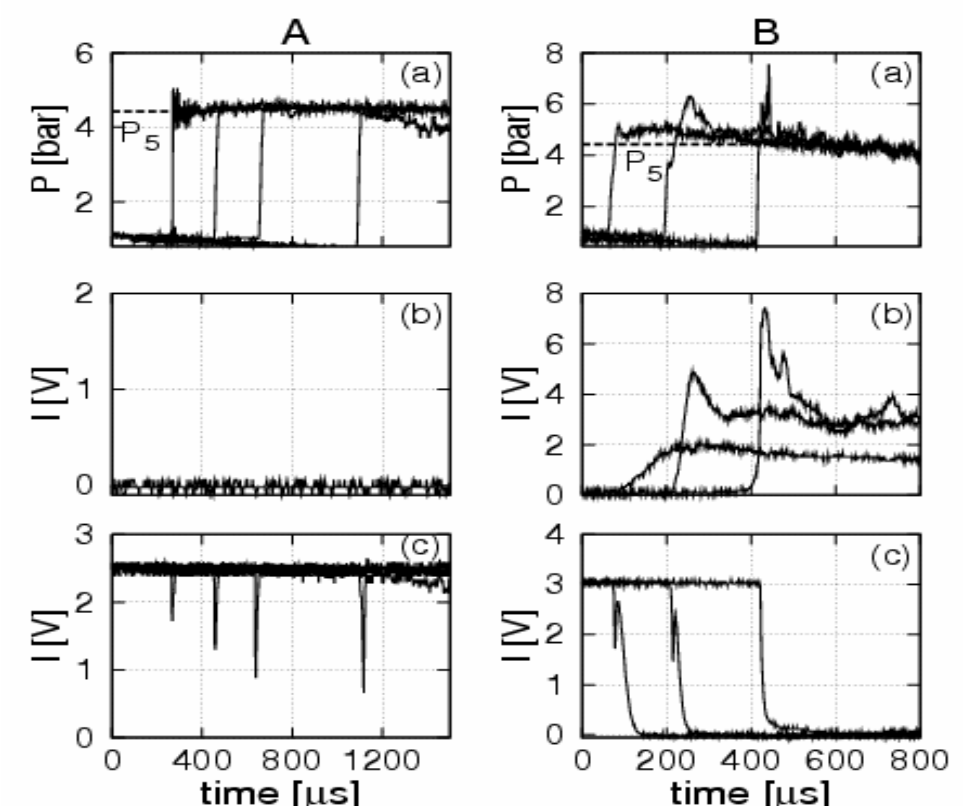


Fig. 2 The time profiles of pressure (a), radiation at 633 nm (b) and laser light attenuation (extinction) (c), measured behind shock waves in the mixtures 10%C_3O_2+Ar at various distances (70 mm, 140 mm and 295 mm) from the end plate of shock tube. The "frozen" temperatures T_5 behind the wave near end plate: A – T_5 = 1390K; B - T_5 = 1620K.

3 Results

The obtained results are illustrated in Fig.3(A,B,C) by the comparison of observed shock wave parameters with the behavior of Hugoniot adiabatic curves [5] for the initial mixtures (curves I) and for the mixtures after condensation (curves II). Straight lines 2 – 5 correspond to calculated velocity of reflected shock wave. Points 6 and rays 2 – 6 represent the experimentally measured pressure

maxima and velocity of accelerated wave front. Points P_{exp} show the steady pressure values and the points C-J demonstrate the Chapman-Jouguet parameters of detonation, calculated in one-dimensional approximation [5].

One can see that in the mixture 10%C_3O_2+Ar (Fig.3A) ray 2 – 6 intersects adiabat II at noticeably less pressures than P_{exp} and measured velocity of the wave is a bit higher than Chapman-Jouguet velocity (tangent to curve II from point 2). This behavior of the wave can be caused by the insufficient heat release resulting in remaining support of the wave propagation by the pressure behind it. Such a flow regime is usually called "overdriven detonation".

In the mixture 20%C_3O_2+Ar (Fig.3B) a very good coincidence of measured and calculated values of pressure and wave velocity is observed. At these conditions the calculated temperature behind the detonation front is 2460 K that according to [4] it corresponds nearly to maximum condensation rate.

In more rich mixture 30%C_3O_2+Ar (Fig.3C) 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 at incomplete condensation at the temperature rise above 2800 K. At these temperatures the reversal processes of particles decay, slowing down the effective condensation rate, begin to play a role. Due to that the energy of condensation can not be completely transmitted to the wave dynamic and so-called regime of damping, "underdriven detonation" is observed.

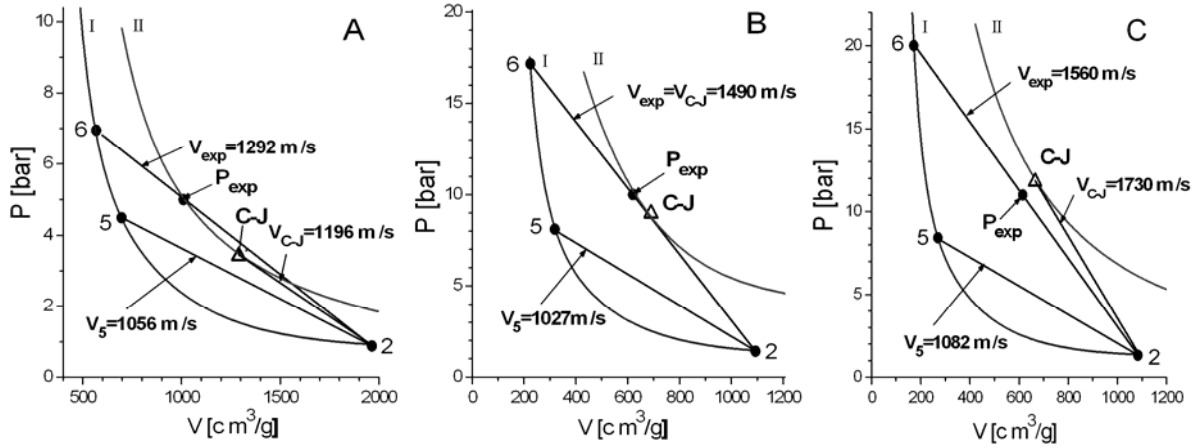


FIG. 3. The behavior of Hugoniot adiabatic curves for the initial mixtures (curves I) and for the mixtures after condensation (curves II). A - mixture 10%C_3O_2+Ar, T_{C-J} = 2050 K; B - mixture 20%C_3O_2+Ar, T_{C-J} = 2460 K; C - mixture 30%C_3O_2+Ar, T_{C-J} = 2830 K.

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