

Inhibition of Spontaneous Decomposition of Acetylene by Hydrocarbon: an Experimental Investigation

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1 Introduction

The problem of effective inhibition of flame and detonation in gases is one of extreme urgency. Environmentally safe and nontoxic inhibitors, i.e., substances which decelerate chemical reactions [1] or terminate them altogether, for example, the process of exothermal spontaneous decomposition, are required for uses in industry. It appears attractive to use a combustible gas as inhibitor, such a gas causes hardly any change in the overall thermal effect of reaction with oxidizer.

One of the promising gas fuels in devices which utilize both deflagration combustion of fuel (welding, cutting of metal) and detonation combustion (sputtering, disintegration) is a mixture of acetylene with air (with oxygen), which is characterized both by a high caloric power and by a short pre-detonation distance, by high parameters of detonation products, and by wide concentration limits of forming of detonation. However, the disadvantage of pure acetylene is its ability to decompose down to the formation of hydrogen and carbon or methane with energy release and possible forming of detonation; this limits the use of acetylene from the standpoint of safety.

If in an acetylene-oxygen torch acetylene is consumed just after its formation from carbide the inhibitor is not required. But if acetylene is accumulated in a big cavity or at elevated pressure (above 2 bar) the inhibition is required. For example, at the moment of ignition of the torch the wave of the decomposition may formed (popping-back). This wave destroys the balloon and equipment. It is necessary to use the inhibitor in a compressor plant and storage plant where acetylene is compressed up to 50 bar. In addition, inhibitor may be used in propulsion systems where higher consumption is required.

The introduction into acetylene of a component which interferes with the process of decomposition enables one to solve this problem. However detonation properties of binary fuel mixtures remains still unclear, in particular for combination of a reactive fuel and a less reactive one [2].

The process of inhibition may be accomplished in the following two ways:

1. by introducing a gas of high heat capacity, which removes a part of energy released in the course of reaction without being involved in the reaction; and
2. by introducing a gas which is involved in chemical reactions and accelerates the loss of active radicals by termination of chains. It is demonstrated in papers dealing with inhibition [3, 4] that, rather than decreasing, the importance of chain avalanche increases with increasing temperature

in the course of combustion. It is known at present [5, 6] that all modes of combustion, including detonation, may be successfully inhibited at atmospheric and elevated pressures; in so doing, the inhibitor efficiency is defined by its ability to terminate reaction chains.

This paper is devoted to experimental determination of the lower concentration limit of inhibitor such as a liquefied propane-butane mixture, at which no spontaneous decomposition of acetylene occurs or hardly any decrease in the overall thermal effect of reaction with oxidizer.

2 Experimental Setup

The experimental investigations were performed in an apparatus fashioned as a cylindrical shock tube with an overall length of 1617 mm and inside diameter of 22 mm (Fig. 1). The shock tube consisted of a detonation combustor (DC) 585 mm long and a measuring section (MS) 1032 mm long separated by a ball cock (BC). The recording equipment included PCB 113A piezoelectric pressure transducers (PT) and FD-256 photodiodes (PD). The spacing between the transducers was 200 mm, and the spacing between the first transducer and spark gap (SG) was 816 mm.

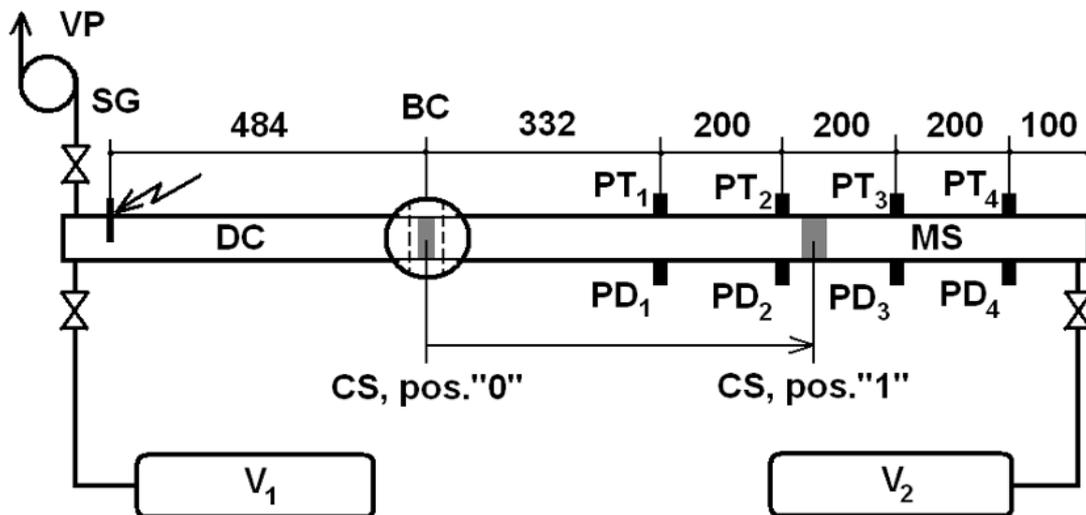


Figure 1: Schematic of the experimental stand: DC - detonation combustor; MS - measuring section; BC - ball cock; VP - vacuum pump; SG - spark gap; PT₁-PT₄ - PCB 113A piezoelectric pressure transducers; PD₁-PD₄ - PD-256 photodiodes; CS - contact surface; pos. "0" and pos. "1" - initial and end positions of the contact surface; V₁ - vessel with stoichiometric acetylene-oxygen mixture; V₂ - vessel with acetylene-inhibitor mixture.

The DC was filled with a stoichiometric acetylene-oxygen mixture to a pressure of 1 bar, and the MS - with an acetylene-inhibitor mixture to the same pressure with closed BC. The DC and MS were pre-evacuated to a pressure of 0.004 bar. The test mixture was composed by the partial pressures of the components with an error of 0.5%. The mixture was held for at least 42 h in a 3-liter vessel at a pressure of 2 bar. After filling, the ball cock was opened, the acetylene-oxygen mixture was ignited by a spark gap, and detonation was further formed. The pre-detonation distance was less than 200 mm, which is much less than the DC length. A detonation wave, which formed in the acetylene-oxygen mixture, passed the contact surface (CS, position "0") from left to right and changed to a shock wave in the test mixture.

The length of MS was selected such that the contact surface would reach the first pair of pressure transducers (PT₁, PT₂) but would not reach the second pair of transducers (PT₃, PT₄). The contact surface stopped at the instant of its interaction with a reflected shock wave behind which the gas is stationary (position "1"). Therefore, the last pair of transducers could register only the glow of decomposing acetylene.

3 Results

Figure 2 gives oscillograms of the shock-wave process occurring in a mixture of acetylene with inhibitor.

In the case where the inhibitor content in acetylene was six percent by volume and less (Fig. 2a), a wave of exothermal decomposition of acetylene (DW) arose. The pressure transducers PT₁-PT₄ registered the incident (SW) and reflected (RSW) shock waves. The PD₁ photodiode registered the arrival of contact surface (CS) and the glow of detonation products of acetylene at the instant of transmission of reflected shock wave. The PD₃ and PD₄ photodiodes registered the intense glow of the wave of acetylene decomposition behind the reflected shock wave. The decomposition wave (DW) propagated in the wake of reflected shock wave.

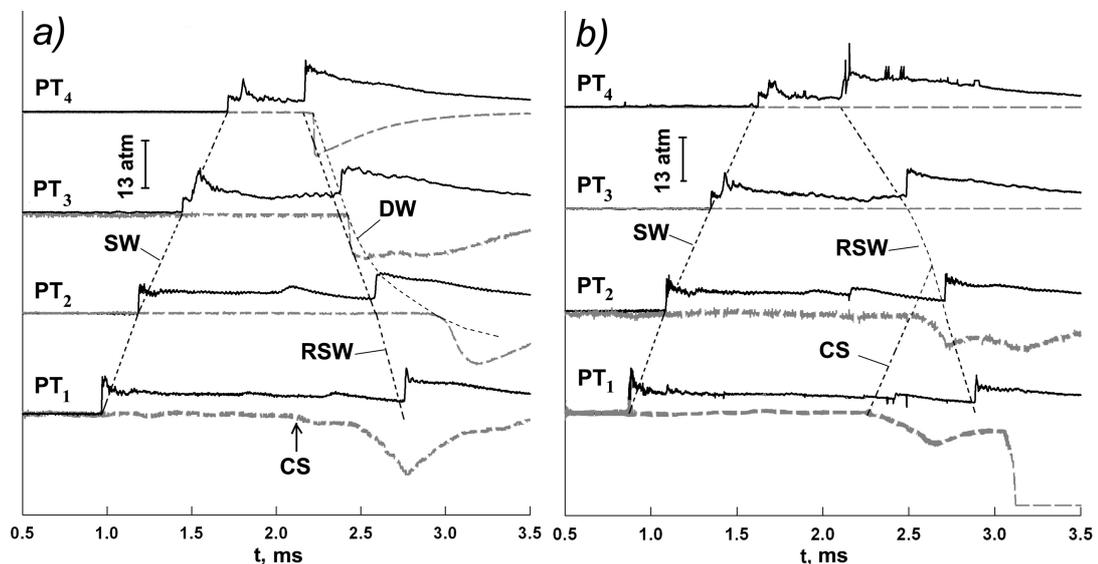


Figure 2: Oscillograms of pressure (solid lines), glow (dash lines) and trajectories of waves and contact surface (dotted lines) in the presence of inhibitor: (a) inhibitor concentration of 6%; (b) inhibitor concentration of 7%; PT - piezoelectric pressure transducers; SW - shock wave; CS - contact surface; DW - decomposition wave; RSW - reflected shock wave.

No spontaneous decomposition of acetylene occurred when the inhibitor concentration was 7% by volume and higher (Fig. 2b). The PD₁ and PD₂ photodiodes registered the arrival of contact surface and the glow of detonation products of acetylene at the instant of transmission of reflected shock wave. However, the PD₃ and PD₄ photodiodes did not register the glow of gas during 20 ms. This is indicative of the absence of decomposition wave in acetylene.

The table 1 gives the measured parameters (except for temperature) of the test mixture behind the incident and reflected shock waves in the position PT₄. The temperature was calculated as a function of Mach number of the incident and reflected shock waves. One can see in the table that the pressure behind the reflected shock wave increased as high as 17 to 28 bar, and the temperature - as high as 800

to 1000 K. In all instances, except for the case of inhibitor concentration of 25%, the conditions of the acetylene-inhibitor mixture behind the reflected and incident shock waves were identical. Therefore, we can speak of the adequacy of the obtained results.

Table 1: Parameters of unreacted gas behind the incident and reflected shock waves in cross section PT_4 : C_{inh} - concentration of inhibitor in mixture with acetylene; M_{SW} - Mach number of incident shock wave (SW); P_{SW} - pressure in the SW front; T_{SW} - temperature in the SW front; P_{RSW} - pressure in the reflected SW (RSW) front; T_{RSW} - temperature in the RSW front.

$C_{inh}, \%$	M_{SW}	P_{SW}	T_{SW}	P_{RSW}	T_{RSW}	
0	$2,18 \pm 0,12$	$5,4 \pm 0,6$	530 ± 29	$11,8 \pm 3,2$	819 ± 66	Presence of decomposition
2,5	$2,44 \pm 0,05$	$6,8 \pm 0,3$	598 ± 18	$16,1 \pm 4,5$	973 ± 29	
5	$2,34 \pm 0,09$	$6,2 \pm 0,5$	570 ± 23	$14,2 \pm 2,2$	911 ± 51	
6	$2,14 \pm 0,07$	$5,2 \pm 0,4$	551 ± 18	$10,7 \pm 2,3$	796 ± 53	
7	$2,06 \pm 0,06$	$4,8 \pm 0,3$	532 ± 21	$9,5 \pm 1,9$	752 ± 48	Absence of decomposition
10	$2,24 \pm 0,09$	$5,7 \pm 0,4$	540 ± 19	$12,2 \pm 0,7$	842 ± 52	
25	2,02	4,6	481	8,1	709	

4 Conclusions

Acetylene has been inhibited by a gas which is a fuel per se. The minimal concentration of inhibitor has been experimentally determined, at which no spontaneous decomposition of acetylene occurred behind reflected shock wave. This minimal concentration was 7%. The thus obtained data may be employed in the case of storage and transportation of acetylene in undissolved state.

References

- [1] Semenov NN (1956). Some Problems in Chemical Kinetics and Reactivity. Moscow: USSR Academy of Science, 686 p.
- [2] Kazuhiro I et.al. (2005) DDT Properties of Hydrocarbon-Air Mixtures with Additive of Acetylene. 20th ICDERS, Montreal, Canada, Paper 112.
- [3] Azatyan VV (1996). Kinetics and Katalysis. V.37, N.4, p.512.
- [4] Azatyan VV et.al. (2006). The Importance of Spontaneous Inhibition on Combustion Processes. Chemical Physics, V.80, N.4, pp.634-639.
- [5] Azatyan VV, Kalanchev VI and Masalova VV (2006). Kinetics and Katalysis, V.47, N.4, pp.498-503.
- [6] Azatyan VV et.al. (2001). Russian Academy of Science Proceedings, V.376, N.1, p.55-58.