Influence of Small Additives of Xe on Detonation Threshold of a Mixture of O_2, H_2 and He

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1.Introduction. Investigations of influence of translational nonequilibrium in the shock wave front on physicochemical processes behind the shock wave are carried out previously (see for example (Genich et al., 1986; 1990; 1992; Kulikov ,1997; 1999; Velikodny and Biturin, 1997; Divakov et al., 2000)). The present study is a continuation of the investigations (Kulikov et al., 2000). Influence of small additive of Xe on the appearance of a detonation in the incident shock wave was investigated depending on the shock wave intensity. The role of translational nonequilibrium was also analyzed in this case.

2. Experimental procedure. The used installation was descried in details in (Genich et al., 1990; 1992). A shock tube was made of a stainless steel and has an inside diameter of 76 mm. It consist of the high-pressure chamber (HPC) (1.5m long) and low-pressure channel (LPC) (4.5 m long). They were separated from each other by a metal diaphragm. HPC was filled up by H_2. LPC was filled up by an investigated gas mixture at room temperature. The pressure p_h in HPC at the moment of breaking of diaphragm was equal to 9.6 atm. Increase of pressure p_l in LPC decreases intensity of the shock wave. The LPC had a measuring section (1m long) at its end.

3. Results of experiments without additive of Xe. Experiments with mixture of $10\%H_2+5\%O_2+85\%$He (mixture I) were performed. (This mixture was used in (Divakov et al., 2000).) Values of the velocity of detonation D are shown by circles in Fig. 1. They are

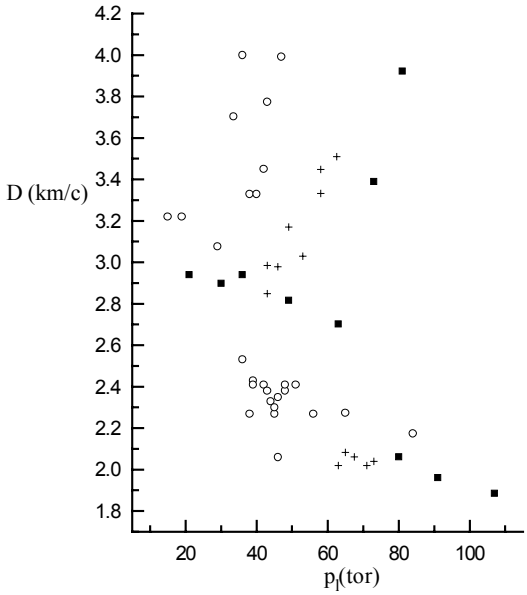

Fig.1.

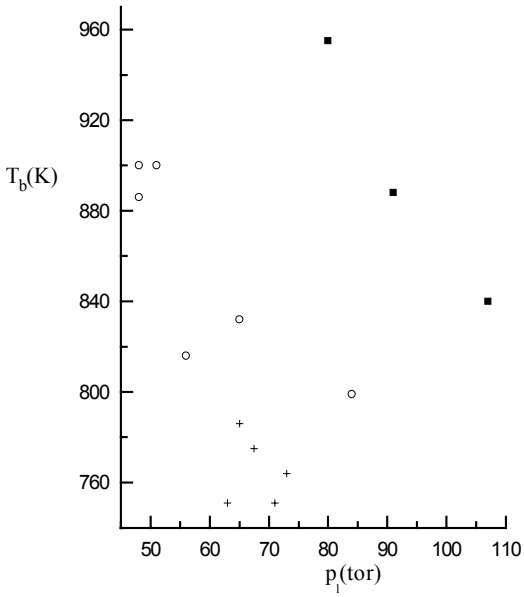

Fig. 2.

obtained for different p_1. Stable detonation was observed at p_1<36 tor. In this case according to emission of OH- particles chemical interaction of O_2 and H_2 develops intensively. Thus, induction period of the interaction τ doesn't exceed 10 μc. The detonation wasn't observed at p_1≥47 tor. And there was no emission of OH - particles. Possibly, it was connected with low value of emission or high value of τ in comparison with the time of arrival of reflected shock wave. Unstable detonation was observed at 36≤p_1<47 tor.

4. Results of experiments with very small additive of Xe. Results change substantially after replacement of 0.5%He by Xe (mixture II, 10%H_2+5%O_2+84.5He+0.5%Xe).Results of these experiments are shown in Fig.1. by crosses. The detonation wasn't observed at p_1≥65 tor. And there was no emission of OH - particles. (In this case Max number of shock wave M was equal to 2.55.) Stable detonation was observed in waves of lower intensity at p_1≤62.5 tor. In this case τ doesn't exceed 10 μc. Unstable detonation wasn't discovered.

Thus, chemical interaction must be faster for the mixture II than for the mixture I. It is next to impossible to replace such a low quantity of He by Xe and to act on chemical and vibrational kinetics or their interaction. But, in this case the mean molecular weight of mixture μ increases by 12%. Probably, this may increase temperature T_b behind the front wave immediately after breaking of diaphragm. The increase of T_b leads to better conditions of detonation formation. In order to get real value of the temperature variation one may use experimental value of D to calculate and compare T_b in the region of p_1 where there is no detonation for both mixtures. Figure 2 shows the values of T_b as a function of p_1 (o - mixture I, +- mixture II). One can see that T_b is lower for mixture II than for mixture I approximately by 40K. Thus, immediately after breaking of diaphragm temperature behind the front wave T_b^s is lower or equal for mixture II in comparison with mixture I. Thus, observed effect doesn't connect with variation of μ.

5. The Monte Carlo statistical simulation of shock wave. According to early carried out numerical investigations (Kulikov, 1997; 1999) we can expect the appearance of stronger translational nonequilibrium in the shock wave front for mixture II in comparison with mixture I. In the front, distribution G_{23} of relative velocities g for pairs containing one molecule of O_2 and one molecule of Xe may exceed substantially its equilibrium value behind the wave. Thus in font, a frequency of high-energetic collisions of molecules O_2 with Xe may considerably exceed its equilibrium value behind the wave. The collisions may lead in front to appearance of considerable amount of high-exciting molecules of O_2 or atoms of O rising as a result of dissociation of O_2 for one collision. This substantially accelerates interaction of O_2 and H_2.

The modeling of a planar stationary shock wave was carried out in an one-dimensional coordinate space and a three-dimensional velocity space. The Monte Carlo method of the unstationary statistical simulation with constant weighting factors was used (Genich et al., 1986; 1992). Molecules were considered as hard spheres. The simulation was carried out for M=2.6 and a mixture of He, O_2 and Xe with the numerical density ratio 189:10:1.The mixture had a composition close to mixture II if to replace H_2 by He. This replacement doesn't affects translational nonequilibrium in the front because the molecular weight of H_2 is less than that of He and the time of rotational relaxation considerably higher than the time of translational relaxation (Genich et al., 1992).

Figure 3 shows the profiles of relative concentrations $n_i^o=(n_i-n_{ia})/(n_{ib}-n_{ia})$ (solid curves: 1-He; 2 - O_2; 3 - Xe) and kinetic temperatures $T_i^o=(T_i-T_a)/(T_b-T_a)$ (dashed curves: 4 - He; 5 - O_2;

6 - Xe) of components. Indices *a* and *b* refer to the variables ahead of and behind the shock wave. The distance *x* along the stream was normalized with respect to the mean free path in undisturbed flow ahead of the wave λ.

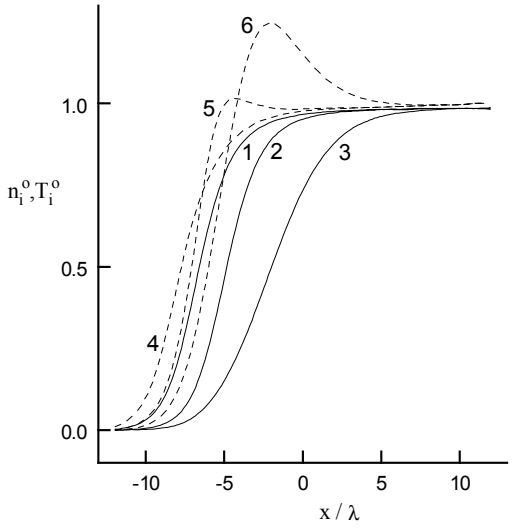

Fig. 3.

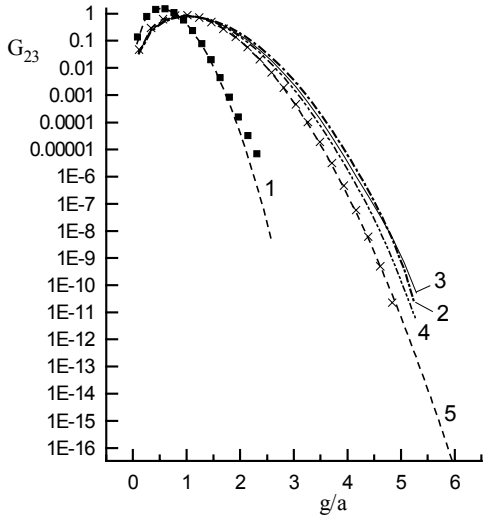

Fig. 4.

Figure 4 shows distributions G_{23}. Velocities are normalized to the sound velocity in the gas mixture ahead of the wave *a*. Curves 1 and 5 are equilibrium G_{23} ahead of and behind the wave. Squares and crosses are distributions obtained at the left and right sides of the modelling region. Curves 2-4 are the G_{22} in the front (2 - x= -3.76; 3 -x = - 2.62; 4 - x= -1.86). As one can see the highest obtained superequilibrium (HOSE) is approximately 300 for G_{23} at the velocity corresponding to one half of the dissociation threshold of O_2 (E_D). Perhaps, the superequilibrium will be considerably greater in the region of higher *g*.

Distributions for pairs of particles of O_2-O_2, He-O_2, He-Xe and Xe-Xe were also obtained. For them values of HOSE were equal to 2.6, 1.6, 2 and 1000, respectively. As one can see they are considerably low than for G_{23} except HOSE for pairs of Xe-Xe. It should be noted that HOSE for pairs of O_2-O_2 and He-O_2 are also obtained at energies substantially low than E_D.

6. Mixture with 2% of Xe. Experiments with mixture of 10%H_2+5%O_2+83%He+2%Xe (mixture III) were also performed. Obtained values of *D* are shown by squares in Fig. 1. Replacement of 2% of He in mixture I by Xe leads to strong shift of boundary of stalling of detonation into region of higher p_l. The sift is stronger than for mixture II. Value of μ increases by 49% for mixture III in comparison with mixture I. As mentioned above, this may lead to increase of T_b.

In order to get real value of the temperature variation calculation of T_b were performed like above. Figure 2 shows by squares the obtained values of T_b. One can see that T_b is higher for mixture III than for mixture I approximately by 140K. Consequently, T_b^s is considerably greater for mixture III in comparison with mixture I. Thus, effect is explained mainly by increase of μ. An influence of the translational nonequilibrium may be also possible.

In order to analyze this the numerical simulation like above was carried out with M=2.6 for mixture of He and O_2 and Xe with the numerical density ratio 93:5:2.The mixture had a

composition close to mixture III if to replace H_2 by He. It was shown that the influence considerably less than for mixture II. Thus, HOSE is approximately 150 for G_{23}. It was realized at g corresponding to one half of E_D. Perhaps, the superequilibrium will be considerably less for mixture III in comparison with mixture II if to make way in the region of higher g. (It should be noted that HOSE for distributions for pairs of particles of Xe-Xe was equal to 100 only.)

7. Conclusion. If to add small amount of heavy molecules (mole fraction less 0.01) then their collisions between themselves occur more seldom than their collisions with molecules of other components. As a result of this frequency of high-energetic molecular collisions of this additive with another less heavy impurity becomes more higher in the front than in equilibrium behind the wave. In this case T_b^s decreases if the ratio p_h/p_l remains constant. Perhaps, this also connects with increase of translational nonequilibrium. Growth of concentration of heavy impurity leads to situation when the number of collisions between themselves becomes substantial fraction of the total number of collisions (mixture III). In this case the effect of superequilibrium decreases and T_b^s increases due to growth of μ if the ratio p_h/p_l remains constant.

Thus, the effect of small additives of Xe on detonation threshold (mixture II) is determined by the feature of translational nonequilibrium in the front.The considered experiment is most convincing and vivid example of appearance of microscopic effect of translational nonequilibrium on macroscopic level.

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