Non-classical detonation regimes of liquid high explosives

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Abstract. This paper presents experimental data of studies of the liquid explosives characteristics, in the reaction zone of which the distribution of parameters does not correspond to the classical detonation theory. An increase of the pressure and particle velocity behind a shock jump in liquid explosives and the possibility of the existence of a steady-state detonation wave without a von Neumann spike are interpreted within the framework of models that take into account the possibility of chemical reactions directly in the shock wave front.

1. Introduction
The authors of the classical theory of detonation [1] Zel’dovich, von Neumann and Doering substantiated the existence of a steady-state detonation wave with the Chapman–Jouguet parameters by considering the specific structure of the reaction zone. In this model, high explosive (HE) without any transformation is pressed in a shock jump to a state lying on its Hugoniot and only then begins to react. One of the conclusions of the theory is the existence of a von Neumann spike in the reaction zone. To date, however, there are a lot of data that cannot be explained within the framework of the classical theory of detonation. For example, authors [2–7] showed that an increase of the pressure in the reaction zone was observed. This phenomenon is due to the high initial reaction rate of heterogeneous HE, which leads to their partial decomposition directly in the shock wave front, and the consequence is the possibility of detonation waves without von Neumann spike. As for liquid HE, which are homogeneous in nature, there is a belief about the low initial reaction rate, and hence the impossibility of the existence of detonation waves without von Neumann spike. Moreover, it is the small chemical reaction rates that destabilize detonation waves in some liquid HE.

The aim of this work is to prove the possibility of chemical reactions directly in the shock wave front in liquid HE, what results in anomalous character of the flow in the reaction zone, as it takes place in pressed HE.

2. Experimental scheme
The liquid HE (nitromethane, tetranitromethane and bis-(2-flouro-2.2-dinitro-ethyl)-formal—FEFO) and their mixtures with not detonating liquids (methanol, nitrobenzene and diethylenetriamine—DETA) were selected as objects of investigation.
Figure 1. Experimental scheme: 1—plane-wave generator; 2—transparent window; 3—aluminum foil; 4—polypropylene shell; 5—ionization gauge.

Figure 2. Particle velocity profiles: 1, 2—the mixture of nitromethane–DETA 99.75 : 0.25; 3—neat nitromethane at the HE–water boundary.

Experimental scheme is shown in figure 1. Detonation in the investigated HE was initiated by a plane-wave generator. Particle velocity profiles were recorded by a laser interferometer VISAR, whose time resolution was 2 ns and velocity measurement accuracy was ±10 m/s. A laser beam was reflected from the 7 µm aluminum foil which was placed between the charge end and the transparent window. The investigated liquid HE was placed in a polypropylene shell with an inner diameter of 36 mm and a wall thickness of 2 mm. The length of the charge was 150 mm. The experimental data represents the velocity of movement of the HE–water boundary and shows all details of the reaction zone structure in the detonation wave. The reliability of the experimental profiles at the use of different materials of window was discussed in [8]. Simultaneously with the particle velocity, the detonation velocity D was measured in each experiment using the ionization gauge, which was the first time-reference point. The second time-reference point corresponded to the beginning of recording of the particle velocity by VISAR. The accuracy of the detonation velocity D measurements was ±0.25%.

3. Experimental results

3.1. Nitromethane

In the experiments for investigation of the reaction zone structure a neat nitromethane (CH$_3$NO$_2$) and its mixture with diethylenetriamine were used. Amines are sensitizers for nitromethane, so even small additions can significantly influence the detonation properties. This is especially evident in the change of the critical parameters [9–11]. It is enough 2 mol % of amine to reduce the critical diameter by seven times [9]. It was expected that the addition of amines should influence the structure of steady-state detonation waves. These studies are especially interesting because low concentrations of amines, exerting strong influence on the kinetics of the decomposition of nitromethane, have little effect on the thermodynamic properties of the solution. Therefore, there is a unique opportunity to investigate the kinetics influence on the character of the flow in the reaction zone, the stability of detonation waves, the possibility of reactions of homogeneous HE directly in the shock wave front, changing only the reaction kinetics of HE.

Measured particle velocity profiles at the HE–water boundary for nitromethane and the mixture of nitromethane–DETA, which contains of 0.25 wt % of DETA are shown in figure 2.
For a fixed composition of a mixture the velocity profiles are reproduced well, and a comparison of curves 1 and 2, which were obtained for two identical experiments, shows this.

There are two most striking features that distinguish the flow in a mixture and neat nitromethane. First, a sharp change in the character of dependence of velocity on time in the reaction zone is observed. In the neat nitromethane behind the shock jump the velocity decreases smoothly and the von Neumann spike in the reaction zone, the duration of which is 50 ns [12], is formed. Moreover, the maximum velocity gradient is realized directly behind the shock wave front. It is this flow that should occur according to the classical theory of detonation [1]. A qualitatively different character of velocity change is recorded in a mixture. After the initial shock jump, it continues to increase for approximately 10 ns, reaches its maximum, and then drops. Second, a small addition of DETA results in substantial quantitative changes in the parameters of the von Neumann spike. For example, its amplitude is reduced by almost an order of magnitude. It should also be noted, that there is not very high, but reliably recorded in the experiments, increase in the Chapman–Jouguet parameters compared to neat nitromethane. Thus, the particle velocity increases by about 50 m/s, and the pressure by 0.4 GPa.

It is impossible to explain the character of those qualitative changes of the flow behind the shock jump, which are observed in the experiments, staying within the classical theory of detonation. In this case, it is necessary to consider the possibility of HE decomposition directly in the shock wave front. This is confirmed by the analysis of the flow in the plane of the pressure $P$ vs the specific volume $V$. The line 1 in figure 3 shows the Hugoniot of neat nitromethane, which is corresponding to the generalized Hugoniot of organic liquids [13]: $D = 1.2C_0 + 1.7u$, where $C_0 = 1.34$ km/s is the speed of sound at zero pressure [14], $u$–particle velocity. The line 2 is the Rayleigh line $P = \rho_0 Du$, $\rho_0 = 1.14$ g/cm$^3$. Experimentally measured parameters of the von Neumann spike in nitromethane (white circle) coincide with the point of intersection of the Rayleigh line and Hugoniot in the limits of experimental error, i.e. a reaction in front can be neglected. Black circle shows the Chapman–Jouguet parameters for neat nitromethane. Method for determination of the parameters in von Neumann spike and Chapman-Jouguet point was considered in detail in [8]. White triangle in figure 3 indicates the value in the von Neumann spike for the mixture of nitromethane with 0.25% of DETA. Hugoniot of this mixture is almost the same as Hugoniot of nitromethane, their Rayleigh lines and the Chapman–Jouguet parameters also coincide within the measurement accuracy. It is seen that in the mixture parameters of the von Neumann spike are much closer to the Chapman–Jouguet point than to the values on the Hugoniot, i.e. HE partially reacts in compression.

### 3.2. Tetranitromethane

The same character of the flow in the reaction zone is observed for tetranitromethane C(NO$_2$)$_4$ mixed with nitrobenzene C$_6$H$_5$NO$_2$. In this case, the tetranitromethane, which has a positive oxygen balance, is an oxidizer, and nitrobenzene is a fuel. Detonation properties of this mixture change no monotonically with increasing of nitrobenzene concentration. In the compositions close to a solution with zero oxygen balance (which corresponds to the ratio of tetranitromethane–nitrobenzene 76.85 : 23.15), detonation velocity reaches a maximum (about 7.5 km/s) and sensitivity to external influences increases [8,15–17]. It can be expected that the rate of chemical reactions increases too.

The obtained particle velocity profiles are shown in figure 4. The numbers indicate the concentration of nitrobenzene in weight percentage. In the neat tetranitromethane, as well as in nitromethane, after the shock jump velocity decreases monotonically and in the reaction zone, the duration of which is about 170±20 ns [12], the von Neumann spike is formed. In the mixture, which contains 15% of nitrobenzene, the velocity after the shock jump continues to increase, and at approximately 10 ns reaches its maximum. The reaction time is reduced to a value, not exceeding 150 ns. Most clear contrast with tetranitromethane is decrease of the amplitude of
Figure 3. The thermodynamic parameters of detonation for neat nitromethane (circles) and at the adding of 0.25% DETA (triangles). 1—the Hugoniot of neat nitromethane; 2—the Rayleigh line.  

Figure 4. The particle velocity histories for neat tetranitromethane (0%) and the mixture of tetranitromethane–nitrobenzene 85 : 15 (15%) at the HE–water boundary. 

The von Neumann spike. Not only the flow in the reaction zone changes noticeably, but also the detonation parameters of the mixture. Detonation velocity increases from 6.4 km/s (for neat tetranitromethane) to 7.27 km/s.

The increase of the Chapman–Jouguet parameters in a mixture is due to increase of the heat of explosion [16]. A sharp decrease of the von Neumann spike amplitude, as well as in the nitromethane, which was considered above, is associated with an increase of the initial reaction rate, causing the HE reaction directly in the shock wave front. This fact becomes evident when considering process in the plane $P$–$V$, shown in figure 5. Solid lines are Hugoniot and the Rayleigh line of tetranitromethane. Hugoniot corresponds to the generalized Hugoniot [13], where the speed of sound at zero pressure is $C_0 = 1.039$ km/s [16], and initial density is $\rho_0 = 1.64$ g/cm$^3$. Experimentally measured parameters of the von Neumann spike in tetranitromethane (white circle) in the limits of experimental error coincide with the point of intersection of the Rayleigh line with Hugoniot, i.e. reaction in front can be neglected. Black circle shows the Chapman–Jouguet parameters for neat tetranitromethane.

The dashed lines in figure 5 show Hugoniot and the Rayleigh line for the mixture of the tetranitromethane–nitrobenzene 85 : 15, the initial density and detonation velocity of which are equal to 1.55 g/cm$^3$ and 7.27 km/s, respectively. For nitrobenzene with initial density of $\rho_0 = 1.2$ g/cm$^3$ the Hugoniot $D = 2.1 + 1.4u$, km/s was used, which satisfactorily described the experimental data [18]. Hugoniot of the mixture was calculated, assuming the validity of the principle of additivity [19]. Black triangle shows the Chapman–Jouguet parameters of the mixture, white triangle—the von Neumann spike parameters. It is seen that in the mixture the von Neumann spike is slightly above the Chapman–Jouguet point and so far from the intersection of the Rayleigh line with Hugoniot, and it can be state about the reaction of most part of HE directly under compression.

3.3. FEFO

Bis-(2-fluoro-2.2-dinitro-ethyl)-formal (FEFO, $C_5H_6N_4O_{10}F_2$) is a powerful liquid HE with an initial density $\rho_0 = 1.6$ g/cm$^3$ and a detonation velocity $D = 7.52$ km/s [20]. In this HE,
Figure 5. The thermodynamic parameters of detonation for neat tetranitromethane (circles) and at the adding of 15% nitrobenzene (triangles).

Figure 6. The particle velocity histories for neat FEFO (0%) and the mixture of FEFO–methanol (15%) at the HE–water boundary.

an unexpected character of the flow in the reaction zone is observed. In liquid HE with a slow kinetics the detonation waves are unstable [21]. It would be expected that this does not apply to FEFO, because it has a relatively small reaction time (about 300 ns [12]). The result, however, was different. Figure 6 shows the velocity profiles for neat FEFO and the mixture of FEFO–methanol 85 : 15. The numbers indicate the concentration of the solvent. Particle velocity profile for FEFO both in the chemical reaction zone and the unloading wave is strongly oscillating, and the characteristic amplitude of oscillations is about 50 m/s. A pronounced period of oscillations is absent, but the order of magnitude is approximately 50 ns. It means that detonation front is unstable and the size of the heterogeneities is comparable to the thickness of 7-micron foil, i.e. it is about 10 microns.

Unlike tetranitromethane, FEFO has a negative oxygen balance, so additions of any inert diluents reduce its detonation parameters and reduce the reaction rate, what should result, according to the traditional view on the structure of detonation waves, in further development of instability. Instead, in a concentration range of methanol from 10% to 15% the flow stabilization is observed. As an example, the velocity profile, obtained at addition of 15% methanol, is shown in figure 6, and, as it can be seen, the oscillations disappear. The velocity gradient in the reaction zone increases, and the sharp velocity drop occurs during the first 50 ns. A high initial reaction rate behind the shock jump results in the stability of the detonation wave. Such an unusual character of the reaction zone structure is due to the partial reaction of HE directly in the shock wave front. This assumption is confirmed by the analysis of the flow in the plane of the pressure–specific volume. Solid lines in figure 7 are the Hugoniot for FEFO and the Rayleigh line. Hugoniot of FEFO, which approximates well the experimental data [22], is \( D = 1.63 + 1.76u \), km/s, and it almost coincides with the generalized Hugoniot of organic liquids \( (C_0 = 1.27 \text{ km/s}) \). Black circle corresponds to the parameters of Chapman–Jouguet, white circle—the von Neumann spike parameters. It is seen that in neat FEFO, the pressure in the von Neumann spike is significantly lower than the value, which corresponds to the intersection of the Rayleigh line with Hugoniot. I.e. due to the high initial reaction rate, a part of HE, which reacted in the shock wave front, is quite high, and in the reaction zone only “afterburning” with a relatively low speed occurs.
Figure 7. Thermodynamic parameters of detonation for neat FEFO (circles) and at the adding of 15% methanol (triangles).

The dashed lines in figure 7 show Hugoniot and the Rayleigh line for the mixture of FEFO–methanol 85 : 15, the initial density and detonation velocity of which are equal to 1.39 g/cm$^3$ and 6.64 km/s, respectively. The generalized Hugoniot was used as Hugoniot for methanol, the speed of sound was equal to $C_0 = 1.12$ km/s [13], $\rho_0 = 0.79$ g/cm$^3$. Hugoniot of the mixture was calculated, assuming the validity of the principle of additivity. Black triangle corresponds to the Chapman–Jouguet parameters, white triangle—the von Neumann spike parameters. It is seen that the von Neumann spike is a little closer to the point of intersection of the Rayleigh line with Hugoniot of the mixture. However, as in the neat FEFO, the part of HE decomposition in the shock wave front remains quite high.

4. Conclusion

The results show that the non-classical detonation regimes are not an exceptional phenomenon. They are observed in experiments not only with pressed (heterogeneous), but with liquid (homogeneous) HE. As already noted, it is impossible to explain the increase of the pressure (particle velocity) after the shock jump with the subsequent formation of the maximum in the framework of the classical detonation theory. The possibility of the existence of a steady-state detonation wave without a von Neumann spike seems impossible too. However, these regimes are observed experimentally and find an explanation in the models that consider the possibility of HE reaction directly in the shock wave front. The authors of [23–25], for example, considered the structure of a steady-state detonation wave in a viscous medium at the presence of the processes of thermal conductivity and diffusion. It was shown that taking into consideration of the shock wave front width and processes in it, including chemical reactions, influences the character of the flow in the reaction zone and results in the possibility of propagation of a steady-state detonation wave without a von Neumann spike and underdriven detonation regimes. Numerical study of the development of detonation in the system with kinetics of exothermic reaction, including dependence on the rate of specific volume change, presented in the works [26, 27], confirms the importance of accounting of reactions in the shock wave front.

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