Detonation properties of the mixtures of tetranitromethane/methanol and tetranitromethane/nitrobenzene

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Abstract. In this work, the reaction zone structure, stability of detonation waves and limits of detonation propagation in the mixtures of tetranitromethane/methanol and tetranitromethane/nitrobenzene depending on the diluent concentration, were studied by a VISAR laser interferometer with a nanosecond time resolution. In the experiments, a sharp change in the reaction zone at the concentration of diluents in the vicinity of stoichiometry is observed – the amplitude of von Neumann spike decreases significantly. This is due to an increase in the initial reaction rate, which leads to the decomposition of HE directly in the shock wave front. It was found that the addition of diluent resulted in an increase in the detonation velocity of the tetranitromethane/diluent mixture in the vicinity of the stoichiometric concentration (about 25% of methanol or nitrobenzene). In almost the entire concentration range, the detonation waves are stable with respect to the formation of the cellular structure of the front. At the same time, in the range of diluent concentration of 15-35%, a poor reproducibility of the amplitude values of the particle velocity from shot to shot is observed. This is probably due to the longitudinal instability of the detonation waves in the mixture.

1. Introduction
Despite the fact that in liquid high explosives (HE) the chemical reaction occurs in a volume, which should simplify the analysis of detonation processes in comparison with pressed HE, in fact, the nature of the flow that occurs during the detonation of liquid HE is often so complex and diverse that it is not possible to even approximate it within the framework of the classical detonation model [1]. In such HE, detonation waves can propagate both in a steady-state and unstable regime [2]. Instability results in the formation of a cellular structure of the detonation front, as well as to the occurrence of reaction failure waves at the edge of the charge. However, even if the detonation is steady-state, the flow in the reaction zone does not always correspond to the classical model of detonation [3]. The character of detonation processes of liquid HE is determined primarily by the activation energy and the thermal effect of the reaction, which can be varied over a wide range by adding inert and chemically active diluents. And we can get information on the effect of the kinetics of chemical reaction on the detonation wave structure and critical parameters. This paper presents the results of an experimental study of mixtures of tetranitromethane (TNM) with nitrobenzene (NB) and methanol (M). TNM is a strong oxidizer with a positive oxygen balance of 49%. Therefore, additives of fuel, which are nitrobenzene and methanol, allow changing the heat of the explosion, and, consequently, the detonation parameters of the mixture [4] and it can be expected that this will result in a significant change in the reaction zone structure. In addition, authors [4-6] note poor reproducibility of experimental data in the mixtures of TNM with some diluents in the vicinity of stoichiometric
concentrations of diluents (zero oxygen balance). The reasons for this phenomenon remain unclear, and in such a situation, the experimental study of the influence of various factors (charge diameter, shell material, conditions of the mixture preparation) on the reproducibility of the particle velocity profiles is very important.

2. The scheme of experiments

The experimental scheme is shown in Fig. 1. The HE charge was placed into the shell (4) from polypropylene, PMMA or steel. The length of charge varied from 50 to 260 mm, the internal diameter of the tube varied from 26 to 50 mm. Shock waves in the investigated mixture were initiated by the pressed charge of TNT/RDX (1). The velocity of the HE-water boundary was recorded by a push-pull VISAR laser interferometer [7]. A laser beam (532 nm) was reflected from an aluminum foil (3) with a thickness of 7-400 μm which was placed between the investigated mixture and optical window (2). In our experiments, the water window is used as an optical one. The experimental data shows the velocity of movement of the HE-water boundary and as result of experiments, the particle velocity profiles are recorded on the HE-water boundary. To determine the absolute value of the particle velocity, two interferometers with velocity fringe constants of 280 m/s and 1280 m/s were used simultaneously. At the same time in each experiment, the ionization gauge (5) recorded the entry time of the detonation wave, which allowed us to determine the value of the detonation velocity \( D \) using interferometric data.

![Fig. 1. The scheme of experiments: 1 — the pressed charge of TNT/RDX; 2 — an optical window; 3 — aluminum foil; 4 — the shell; 5 — the ionization gauge.](image)

3. Experimental results

In the experiments, TNM (C(NO\(_2\))\(_4\)) with 1.64 g/cc initial density and 6.48 km/s detonation velocity, methanol (CH\(_3\)OH) and nitrobenzene (C\(_6\)H\(_5\)NO\(_2\)) with 0.79 g/cc and 1.20 g/cc initial densities were used. For each concentration of diluent, from 3 to 20 experiments were performed. Typical particle velocity profiles for TNM/M recorded at the HE-water boundary are shown in Fig. 2. For pure TNM, the velocity change over time corresponds to the classical model of detonation (Fig. 2, profile 1) - the velocity after the initial shock jump decreases, and the von Neumann spike is formed in the reaction zone. The transition from the reaction zone to the unloading wave is smooth, so that it is impossible to uniquely find the Chapman-Jouguet (CJ) point on the velocity profile. Nevertheless, the problem of determination of the CJ point position can be solved unambiguously [8]. It is worthwhile to try changing parameters of the experiment, for example, the charge diameter, the length of the charge, or conditions of detonation initiation. If the diameter is much greater than the critical one, the flow in the reaction zone remains constant, while the velocity gradient in the unloading wave depends on these varying parameters of the charge. In our experiments, we changed the flow in the unloading wave by...
varying the length of the charge at a fixed diameter [8]. The value of the characteristic reaction time was equal to 175±25 ns. The parameters of von Neumann spike were found by analysis of shock waves interaction in the pressure $P$ – particle velocity $u$ plane [8, 9]: $u_N = 2.52 ± 0.06$ km/s, $P_N = 26.5 ± 0.6$ GPa. The obtained values of velocity and pressure at the CJ point are 1.55±0.02 km/s and 16.5±0.2 GPa, respectively, which are approximately 1.6 times less than that of von Neumann spike. These values agree well with the data [2, 5, 10].

3.1. The mixture of tetranitromethane/methanol

The results for the TNM/M mixture are qualitatively different - the addition of methanol results in the decrease of amplitude of Von Neumann spike, whereas detonation parameters increase (Fig.2). The addition of diluent significantly increases the initial reaction rate of the TNM/M mixture, and as a result, HE begins to react directly in the shock wave front, which leads to the disappearance of the von Neumann spike. This is confirmed by the increase in the velocity after the shock jump and the formation of a character maximum in the vicinity of ten nanoseconds, which is observed on all velocity profiles in the range of methanol concentrations of 15-35%. When the methanol concentration does not exceed 40%, the recorded velocity profiles are smooth, without any oscillations. This means that detonation waves in pure TNM and its mixtures with methanol are stable with respect to disturbances, which leading to the formation of a cellular structure. A further increase in methanol concentration results in the appearance of oscillations on the velocity profiles (Fig. 2, profile 5), which indicates the instability of the detonation front.

Simultaneously with the particle velocity in the experiments, the detonation velocity $D$ was recorded. The dependence of detonation velocity of the TNM/M mixture on the methanol concentration is shown in Fig.3. In pure tetranitromethane, the detonation velocity is equal to 6.48 km/s. When methanol is added, it increases to 6.76 km/s at a methanol concentration of 10% and remains almost constant until the stoichiometric concentration of the TNM/M mixture (75.4/24.6). In the vicinity of stoichiometry, at a small negative oxygen balance $D$ reaches a maximum value of 6.90 km/s and decreases with further dilution. The critical concentration of methanol $C_{cr}$, above which the detonation in the TNM/M mixture does not propagate, is equal to 62%.

![Fig. 2. Particle velocity profiles on the TNM/M – water boundary for different concentration of methanol: 1 – 100/0; 2 – 90/10; 3 – 85/15; 4 – 72/28; 5 – 50/50. Al foil thickness is equal to 7 µm.](image)

The detonation parameters of the mixture of TNM/M obtained in the experiments are shown in table 1. Density of the mixture $d$, detonation velocity $D$, particle velocity $u$ and pressure $P$ at the CJ
point depending on the methanol concentration are presented. Table 1 shows the measurement error of $u$ and $P$, which is mainly due to the uncertainty of the position of the CJ point on the particle velocity profiles for all mixtures except pure TNM. In addition, the spread of $u$ and $P$ parameters in the 15-35% of methanol concentration range is associated with poor reproducibility of the results. This phenomenon will be described below.

Table 1. The detonation parameters of the mixture of TNM/methanol.

| Wt. % TNM/M | $d$, g/cc | $D$, km/s | $u_{CJ}$, km/s | $P_{CJ}$, GPa |
|------------|-----------|-----------|---------------|---------------|
| 100/0      | 1.64      | 6.48      | 1.55±0.01     | 16.5±0.1      |
| 90/10      | 1.48      | 6.76      | 1.87±0.05     | 18.7±0.5      |
| 85/15      | 1.41      | 6.79      | 1.90±0.10     | 18.2±0.9      |
| 80/20      | 1.35      | 6.79      | 1.95±0.08     | 18.0±0.8      |
| 78/22      | 1.33      | 6.82      | 2.00±0.05     | 18.1±0.5      |
| 75/25      | 1.29      | 6.85      | 1.98±0.05     | 17.5±0.5      |
| 74/26      | 1.28      | 6.88      | 1.95±0.03     | 17.2±0.3      |
| 73/27      | 1.27      | 6.90      | 1.95±0.03     | 17.1±0.3      |
| 72/28      | 1.26      | 6.83      | 1.93±0.03     | 16.6±0.3      |
| 70/30      | 1.24      | 6.79      | 1.90±0.03     | 16.0±0.3      |
| 65/35      | 1.19      | 6.58      | 1.80±0.03     | 14.1±0.3      |
| 60/40      | 1.15      | 6.36      | 1.80±0.02     | 13.2±0.2      |
| 50/50      | 1.07      | 5.91      | 1.72±0.02     | 10.9±0.2      |
| 40/60      | 1.00      | 5.41      | 1.62±0.02     | 8.8±0.1       |

Fig. 3. The experimental dependence of detonation velocity of the TNM/M mixture on the methanol concentration.
3.2. The mixture of tetranitromethane/nitrobenzene

As in the mixture of TNM/M, the adding NB to TNM results in the decrease of amplitude of von Neumann spike, whereas detonation parameters increase. At 5% and 10% of nitrobenzene, the decrease in the amplitude of von Neumann spike is noticeable, and beginning from 15%, it is difficult to talk about von Neumann spike in the chemical reaction zone, because after the initial shock jump, the particle velocity continues to increase, for approximately 10 ns, reaches its maximum, and only then begins to decrease (Fig. 4).

![Particle velocity profiles on the TNM/NB – water boundary for different concentration of nitrobenzene. Al foil thickness is equal to 7 µm.](image)

**Fig. 4.** Particle velocity profiles on the TNM/NB – water boundary for different concentration of nitrobenzene. Al foil thickness is equal to 7 µm.

With a further increase in the concentration of nitrobenzene, the qualitative character of the dependence of the particle velocity on time remains unchanged, while the growth of the detonation parameters of the TNM/NB mixture continues (Fig. 4). The maximum values of pressure $P_{CJ}$ and particle velocity $u_{CJ}$ are observed at the concentration of nitrobenzene equal to 30% (at small negative oxygen balance). The subsequent increase in the amount of NB reduces the detonation parameters of the TNM/NB mixture. Moreover, at 50% NB, von Neumann spike begins to appear again in the reaction zone, although its amplitude is much less than for pure TNM. The loss of stability is observed near the critical concentration of nitrobenzene $C_{cr} = 76\%$, above which the detonation in the TNM/NB mixture does not propagate.

The dependence of detonation velocity of the TNM/NB mixture on the nitrobenzene concentration is shown in Fig. 5. When nitrobenzene is added, detonation velocity increases to approximately 7.5 km/s in the vicinity of the stoichiometric concentration of the TNM/NB mixture, equal to 76.8/23.2, and decreases with further dilution. The minimum detonation velocity, 5.62 km/s, was recorded at the concentration of 75% nitrobenzene.

The experimental detonation parameters of the mixture of TNM/NB are presented in table 2. Given values of $D$, $u_{CJ}$, and $P_{CJ}$ are averaged one.
Fig. 5. The dependence of detonation velocity of TNM/NB on NB concentration. Filled circles – our experimental data; solid line is their approximation; the empty triangles and squares relate to previously published data: Δ - [4] and □ - [11].

Table 2. The detonation parameters of the mixture of TNM/nitrobenzene.

| Wt.% TNM/NB | d, g/cc | D, km/s | u_CJ, km/s | P_CJ, GPa |
|-------------|--------|---------|------------|-----------|
| 100/0       | 1.64   | 6.48    | 1.55±0.02  | 16.5±0.2  |
| 95/5        | 1.61   | 6.88    | 1.57±0.03  | 17.4±0.3  |
| 90/10       | 1.58   | 7.09    | 1.63±0.05  | 18.3±0.5  |
| 85/15       | 1.55   | 7.27    | 1.85±0.08  | 20.9±0.9  |
| 82/18       | 1.54   | 7.32    | 1.92±0.05  | 21.6±0.6  |
| 80/20       | 1.53   | 7.53    | 1.84±0.05  | 21.1±0.6  |
| 78/22       | 1.52   | 7.47    | 1.91±0.05  | 21.7±0.6  |
| 76/24       | 1.51   | 7.50    | 1.97±0.07  | 22.3±0.8  |
| 74/26       | 1.50   | 7.52    | 2.09±0.05  | 23.6±0.6  |
| 72/28       | 1.49   | 7.48    | 2.29±0.04  | 25.5±0.5  |
| 70/30       | 1.48   | 7.48    | 2.38±0.04  | 26.3±0.5  |
| 65/35       | 1.45   | 7.30    | 2.34±0.04  | 24.8±0.5  |
| 60/40       | 1.43   | 7.05    | 2.23±0.04  | 22.5±0.4  |
| 55/45       | 1.41   | 6.86    | 2.07±0.03  | 20.0±0.3  |
| 50/50       | 1.39   | 6.70    | 1.90±0.03  | 17.7±0.3  |
| 40/60       | 1.34   | 6.30    | 1.67±0.03  | 14.1±0.3  |
| 35/65       | 1.32   | 6.08    | 1.50±0.03  | 12.0±0.3  |
| 30/70       | 1.31   | 5.85    | 1.37±0.03  | 10.5±0.3  |
| 25/75       | 1.29   | 5.62    | 1.26±0.02  | 9.1±0.2   |
4. The reproducibility of experimental data and conclusion
The poor reproducibility of experimental data in the mixtures of TNM with methanol and nitrobenzene in the vicinity of stoichiometric concentrations of diluents was observed, but not in relation to detonation velocity. In the whole range of existence of detonation in the mixture of TNM/diluent, \( D \) was recorded within the experimental error. At the same time, it was also found that there was some discrepancy between particle velocity profiles for the same concentration of the mixture, which were obtained in different tests. Fig. 6 shows four particle velocity profiles for the mixture of TNM/M 85/15. In all the experiments, the parameters of experimental assemblies and ambient condition were the same. It can be seen that the discrepancy between profiles is about 250 m/s, what exceeds the experimental error. It is noteworthy that detonation velocity is the same in all experiments, \( D = 6.79 \pm 0.03 \text{ km/s} \).

![Particle velocity profiles for the mixtures of TNM/M 85/15.](image)

This phenomenon may be connected with the lack of the front flatness or the longitudinal instability in the TNM/diluent mixture. For justifying the flatness of the detonation front, the experiments with recording of particle velocity profiles from several points on the front were performed. Unlike the scheme for previous experiments, a multi-channel VISAR interferometer was used in that case. The results of two shots are presented in Fig. 7. In these experiments, the mixture of TNM/M 85/15 was used, which was placed into the shell from PMMA with the internal diameter of 36 mm, wall thickness of 2 mm and the length of 160 mm. It is seen that three particle velocity profiles obtained from different points on the front coincide within the experimental error. It means that the detonation front is flat. The similar results were observed in other experiments in the same conditions, but the amplitude of particle velocity differs from shot to shot, as it was recorded previously by one-channel VISAR interferometer (Fig. 6). Therefore, the poor reproducibility of detonation parameters in the TNM/diluent mixture may be connected with instability with respect to longitudinal perturbations, in which the perturbed flow, like the initial one, remains one-dimensional with a flat detonation front. In [12, 13] it is noted that the criterion of stability of the detonation waves in relation to longitudinal perturbations depends not only on the activation energy, but also on the heat of
reaction. Detailed studies [14, 15] confirm this conclusion in general, but the quantitative criterion for the stability of detonation waves is much more complex. Recorded in this work difference in the amplitude values of the particle velocity, reaching 10%, agrees with the assumption of longitudinal instability of detonation waves. The absence of equally noticeable changes in the detonation velocity is probably due to a sufficiently large measurement length (at least 70 mm), which leads to averaging of oscillations. The question of the processes of propagation of detonation waves in the range of poor reproducibility of particle velocity profiles requires further research.

![Graph](image.png)

**Fig. 7.** Particle velocity profiles for TNM/M 85/15 recorded in two shots. 
Al foil thickness is equal to 7 µm.

Our investigations also show that in the mixtures of tetranitromethane with methanol and nitrobenzene, significant changes in the structure of detonation waves occur when the diluent concentration is close to the stoichiometric one. Adding diluent to the TNM significantly increases the initial reaction rate of the mixture, as a result of which HE begins to react directly in the shock wave front, which leads to the disappearance of von Neumann spike. On all velocity profiles in the range of diluent concentration of 15-35%, the increase in velocity after the shock jump and the formation of a characteristic maximum in the vicinity of ten nanoseconds is observed. By the time the maximum is reached, a significant part of HE reacts, since according to the data [4], the failure diameter for a stoichiometric mixture of TNM/NB 76.85/23.15 is approximately 0.05 mm, and the reaction time for HE with such a failure diameter is in the order of 10 ns.

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