Calculated estimations of the performance for TKX-50 based formulations

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Abstract. A computational study of the detonation characteristics of several explosive formulations based on the energetic material TKX-50 has been carried out. Materials such as paraffin, HTPB, GAP, AMMO and BAMO were considered as fillers or binders. The influence of such fillers (with a volumetric content of up to 50%) on the detonation characteristics of the composite energetic materials was investigated. The influence of porosity on the detonation characteristics of composite explosive formulations with a binder mass content of 5 and 10% was determined. An analysis of the (limited) experimental data for the detonation velocity of explosive formulations based on TKX-50 was undertaken. The experimentally determined detonation velocities of three explosive formulations with inert and energetic binders which have been previously published in the literature were considered and analysed. Good agreement was found between the calculated and experimental results for the detonation velocity. A computational study of the explosion impact of charges of TKX-50, as well as of explosive formulations based on it containing the above-mentioned binders, on copper plates with a thickness of 1 mm and on layers with a thickness of 50 mm was carried out. The mass content of binders in the explosive formulations was 5%. The charges were 50 mm thick and consisted of compact or porous materials with a porosity of 2%. The Explo5 and Ansys Autodyn programs were used to perform thermochemical, thermodynamic and gas-dynamic calculations.

1. Introduction
The energetic material TKX-50 (dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate) is one of the most interesting new energetic materials that has been developed in recent years [1]. TKX-50 shows a combination of low shock and friction sensitivity with high thermal stability, density and detonation velocity. In addition, it can be prepared by an easy, inexpensive synthesis starting from commonly available starting materials, and shows low toxicity, which makes it attractive for use as a future high-performance explosive with increased safety. Interest in TKX-50 has been significant since the first publication describing its synthesis [2] and various physicochemical properties [2], and a significant number of subsequent works by many research groups have further investigated many aspects of the properties of this energetic material. As an explosive compound, TKX-50 is extremely powerful, and at the same time has the necessary thermal stability, low toxicity and low sensitivity which is required for modern energetic materials. Its various physical and chemical properties have been determined using X-ray diffractometry, nuclear magnetic resonance, infrared spectroscopy and differential scanning calorimetry amongst other techniques. In addition, the sensitivity of TKX-50 towards impact, friction and electrostatic discharge have been determined.

However, interestingly, the basic explosive and technological properties, which must be known in order to create real explosive formulations, has not aroused the same wide interest and remain relatively...
poorly investigated. Therefore, reliable experimental information, which can be used for the creation of specific explosive formulations is currently sparse, and in fact, it is insufficient to advance practical work in this direction. In order to counteract this problem, a series of studies regarding the calculated prediction of the detonation characteristics of some possible composite explosive formulations with inert or energetic binders has been undertaken.

In order to achieve this, the relevant properties of TKX-50 as well as of possible binders must be known. In particular, the standard enthalpy of formation of TKX-50 must be known with confidence. However, various authors have proposed several estimated and experimental values for the heat of formation for TKX-50. Two experimental values have been reported, with the value of 194.1±0.9 kJ/mol being of greatest interest, which was obtained and rechecked in [3-5] by the researchers of an excellent Russian thermochemistry group. The second experimental value of 113.97±2.86 kJ/mol, as well the value of 111±16 kJ/mol obtained in [6, 7] by the Sinditskii group caused a certain bewilderment from the very beginning. Regarding these results, the authors of [4] pointed out, "The presented data testify to bad quality of the used calorimetric equipment and low professional level of authors".

A comparative study of the detonation characteristics and explosive properties of a number of composite explosive compositions based on TKX-50 was carried out in this work. Two inert binders, namely paraffin and HTPB (hydroxyl terminated polybutadiene), as well as three energetic binders - GAP (glycidyl azide polymer), Poly-AMMO (poly-3-azidomethyl-3-methyloxetane) and Poly-BAMO (poly-3-3-bis (azidomethyl) oxetane) were used in the calculations which were performed. The properties of these compounds which are required for thermochemical calculations are given in table 1 and were obtained from many sources in the literature, mainly from [8-13].

| Property | TKX-50 | BAMO | GAP | AMMO | Paraffin | HTPB |
|----------|--------|------|-----|------|----------|------|
| formula  | C₂H₄N₁₀O₄ | C₃H₆N₆O | C₃H₅N₂O | C₃H₅N₂O | CH₂ | C₁₀H₁₅₄Oₙ₀₇ |
| ρ₀, g/cm³ | 1.877 | 1.30 | 1.29 | 1.06 | 0.90 | 0.92 |
| ΔHᵣ, kJ/mol | 194.1 | 413 | 142.3 | 179 | -30.6 | -51.88 |

2. Computational results
As was noted in the introduction, one of the most important values for conducting such a study is an accurate value for the enthalpy of formation of TKX-50. We have the experimental value of the enthalpy of formation obtained by credible researchers, and fragmentary experimental data on the detonation velocity and on the limiting possibilities of compaction for several explosive formulations [14-16]. An explosive formulation of 97% TKX-50 and 3% paraffin was studied in [14], which will be designated as formulation 1 in this work. In [15], additional data were given for formulation 1, and another explosive composition was also studied which consisted of 95.5% TKX-50, 3% ETEP binder (energetic thermoplastic binder), and 1.5% graphite, and is designated as formulation 2 in this work. In [16], an explosive formulation of 94.5% TKX-50, 4.5% paraffin, and 1% graphite was studied, which is designated as formulation 3 in this work.

In [14], five samples of formulation 1 with dimensions of ø30x30 mm compacted to different densities (ρ) were used to measure the detonation velocity (D). It should be noted, that the detonation velocity measurements performed in [14] were carried out according to the method recommended for use in the Chinese military standard GJB772A-97 702.1. The scheme for measuring the detonation velocity using this standard method is found in [17]. An important condition for measuring the detonation velocity using this method, as, indeed, in all normal measurement methods used for this purpose, is a significant separation in distance of the first measuring contact from the place of initiation of the test sample by the booster charge. A linear regression dependence of the detonation velocity on the density of the samples was given in the form \( D = 499 + 4814\rho, R^2 = 0.9925 \). When the authors extrapolated this linear dependence to the theoretical density value for a compact explosive composition, they obtained a detonation velocity of 9260 m/s. In a subsequent calculation using the Urizar formula
[18], they determined the detonation velocity for pure, compact TKX-50 to be 9432 m/s. Some additional results for formulation 1 were reported in reference [15]. These are the values of the densities of all five tested samples of formulation 1 [14] and the values of the detonation velocities recorded for them. The linear regression dependence $D = 149.7 + 5034.8\rho$, $R^2 = 0.9975$ reported based on that data differs slightly from the dependence given in [14, 15].

In order to study of the effect of density on the detonation characteristics of formulation 1, calculations were carried out using the thermochemical program Explo5 [19]. The values for the properties of substances required for the calculations are given in table. 1. The results were calculated for both the densities of the samples tested in the experiments, and for a number of additional density values, which is necessary in order to obtain a more complete picture of the phenomenon under investigation. The calculated results obtained for the effect of the density of formulation 1 on the detonation velocity are shown in figure 1, and are compared with the experimental results [14].

![Figure 1. Influence of the density of explosive formulations 1 (left) and 2 (right) on the detonation velocity: rhombuses - calculation, squares - experiment.](image)

The data presented in figure 1 show that there is extremely good agreement between the calculated and experimental results for the detonation velocity of composition 1. Therefore, it was concluded that other detonation characteristics of the explosive composition should also have been determined in the calculation quite accurately. Formulation 2 in figure 1 is more complex (three components, energetic binder, graphite) shows a slightly worse agreement between the more linear calculated and obviously more erratic experimental data. Moreover, a more general conclusion follows, that the calculation method used is quite reliable, and also, that the properties of the energetic material TKX-50 used in the calculation – and in particular the enthalpy of formation – are qualitative and reliable.

In [15], the main focus of the study was the explosive formulation 2. Attention was paid to the preparation of the TKX-50 powder by grinding it, and in the subsequent preparation of the samples. The grinding of the powder was carried out on the basis that finer powder is better compacted. Samples from formulation 2 were compacted at a pressure of 300 MPa. The density of the samples in this case was 1.79–1.81 g/cm$^3$ and to some extent correlated with the size of the samples. The sizes of samples ranged from ø20×20 mm to ø60×60 mm. Thermochemical calculations of the detonation characteristics of composition 2 were carried out for both, for the density values of the of the samples tested in the experiments performed in [15], and also for a number of additional density values. The energetic glycidyl azide polymer (GAP) was used in the calculations as the energetic thermoplastic binder (ETPE). The calculated results obtained for the effect of the density of composition 2 on the detonation velocity are shown in figure 1.

Explosive formulation 3 was studied in the literature [16] and consists of 94.5% TKX-50, 4.5% paraffin, and 1.0% graphite. The morphology of the TKX-50 powder was considered, and the average particle size was 331 μm. Samples of formulation 3 which were 21 mm in diameter and 12 mm in height
were pressed with a force of 58 kN to a density of 1.725 g/cm$^3$. The results of several experiments which were performed to measure the detonation velocity, found an average value was 8234 m/s with a very small scatter. Thermochemical calculations of the detonation characteristics of composition 3 were carried out, and the reasons for the lower experimental value of the detonation velocity were elucidated in [20] when carrying out a large series of preliminary calculations for all experimentally investigated explosive formulations and their complete analysis. The results of the analysis of the limiting compaction of explosive formulations at pressures up to 300 MPa were also presented [21].

In order to study the effect of the addition of the above-mentioned binders on the detonation characteristics of composite energetic materials based on TKX-50, two series of calculations were carried out using the Explo5 program. It should be noted that the Explo5 program uses a modified, more accurate BKWN-M form of the Becker-Kistiakowski-Wilson equation. The first series of calculations can be conditionally characterized as methodological. Here, in the range of the content of these binders up to 50 vol%, the dependences of the main detonation characteristics of the energetic materials on the volumetric and mass content of the filler are obtained.

In figure 2, the velocity ($D$) and detonation pressure ($P$) are given as the main detonation characteristics, and the volumetric content $\varphi_t$ is indicated for TKX-50. The volumetric content of the filler in this case is determined as $\varphi_f = 1 - \varphi_t$.

In the second series of calculations, which can be conditionally characterized as technological, the detonation characteristics of all composite explosive formulations based on TKX-50 and containing 5 and 10 wt% of the indicated binders were calculated. In this case, the formulations were considered with an initial porosity of up to 10%. In figure 3, the values obtained for the detonation velocity and pressure for a specific explosive formulation (composition) are given for 5 wt% binders depending on its volumetric content in the sample $\varphi_c$, or on its porosity $\pi_c = 1 - \varphi_c$. 

**Figure 2.** Influence of TKX-50 volumetric content on detonation velocity (left) and detonation pressure (right) of composite energetic materials with BAMO (rhombuses), GAP (blue squares), AMMO (triangles), paraffin (blue rhombuses), HTPB (squares) and of only TKX-50 (circles).
Figure 3. Influence of volumetric content (porosity) on detonation velocity (left) and detonation pressure (right) of composite explosive formulations with 5 wt% BAMO (rhombuses), GAP (blue squares), AMMO (triangles), paraffin (blue rhombuses) and HTPB (squares).

The nature of the change in the composition of detonation products with a change in the content of components is also of certain interest for the composite energetic materials under consideration. A sufficiently accurate quantitative experimental determination of the composition of the detonation products at the Chapman-Jouguet point is practically unrealizable, but thermochemical calculation methods make it possible to determine its dependence on the content of the initial components not only at the Chapman-Jouguet point, but also during the entire unloading process until atmospheric pressure is reached. Table 2 compares the compositions of the detonation products at the Chapman-Jouguet point for TKX-50, as well as for explosive formulations based on TKX-50 with 5 wt% of the considered binders. The changes in the content of the main detonation products on gradual transition from TKX-50 to an inert binder HTPB are immediately evident.

As a result of the calculations which were performed, important thermodynamic relations were also obtained. They are equations of state for detonation products in the form of Jones-Wilkins-Lee (JWL). This equation of state is one of the main equations for performing calculations for various explosive processes and is widely used in the practice of gas-dynamic calculations. The expansion isentrope of detonation products for this equation of state has the form

\[ P = A \exp\left(-R_1 V\right) + B \exp\left(-R_2 V\right) + C V^{-\left(1 + \omega\right)}. \]

The coefficients indicated in the above formula were determined from the thermodynamic calculations which were performed and are given in table 3 for TKX-50, as well as for explosive formulations based on TKX-50 containing 5 wt% binders. The calculated detonation characteristics of the explosive substances under consideration are also indicated in the lower part of the table.
Table 2. Composition of detonation products at the Chapman–Jouguet point for compact TKX-50 and explosive formulations with 5 wt% of the indicated binders.

| Formulation Product | TKX-50 Mol % | BAMO Mol % | GAP Mol % | AMMO Mol % | Paraffin Mol % | HTPB Mol % |
|---------------------|--------------|------------|-----------|------------|----------------|------------|
| N₂                  | 46.4032      | 44.1488    | 43.8070   | 43.0063    | 40.0258        | 40.3569    |
| H₂O                 | 32.7348      | 31.2450    | 31.6653   | 31.6077    | 31.2101        | 30.9424    |
| C(s,d)              | 15.8278      | 18.9083    | 18.8724   | 19.2755    | 21.5908        | 21.9971    |
| CH₃O₂               | 1.7659       | 1.2532     | 1.3229    | 1.1894     | 0.7990         | 0.904      |
| NH₃                 | 1.4825       | 2.2137     | 2.0926    | 2.4168     | 3.5574         | 3.0793     |
| CO                  | 0.5538       | 0.5576     | 0.5877    | 0.5895     | 0.3354         | 0.4283     |
| CO₂                 | 0.5433       | 0.8629     | 0.8396    | 0.9919     | 1.1938         | 1.1493     |
| CH₄                 | 0.4531       | 0.3120     | 0.3448    | 0.3068     | 0.1568         | 0.2043     |
| C₂H₆                | 0.1787       | 0.3806     | 0.3581    | 0.4721     | 0.8719         | 0.7263     |
| HCN                 | 0.0244       | 0.0663     | 0.0599    | 0.0858     | 0.2051         | 0.1553     |
| C₃H₄                | 0.0240       | 0.0347     | 0.0339    | 0.0379     | 0.0278         | 0.0322     |
| N₂H₄                | 0.0055       | 0.0127     | 0.0118    | 0.0158     | 0.0212         | 0.0201     |
| CH₃OH               | 0.0004       | 0.0007     | 0.0007    | 0.0008     | 0.0009         | 0.0009     |
| H                   | 0.0001       | 0.0002     | 0.0002    | 0.0002     | 0.0010         | 0.0011     |

The calculated study of the explosive effect of TKX-50 on barriers had been previously investigated [22], but it was later found that the estimated value of the enthalpy of formation of the material had been overestimated. Since the overestimation of the enthalpy of formation naturally leads to overestimated results for the detonation characteristics of the explosive, and consequently, to overestimated parameters of the explosive loading of barriers, the previous work was discontinued. At present, in connection with the improvements, which have been made in the values for certain properties of TKX-50, this work has been resumed, and some of the results obtained are presented below.

In the calculations, explosive charges were calculated containing the energetic material TKX-50 and formulations based on TKX-50, which contained a mass content of binders of 5%. To determine the limiting theoretical capabilities of the explosives under consideration, the charges were taken to be compact, and to determine the limiting practical capabilities, their minimum possible limiting porosity of 2% was set. One-dimensional calculations of the impact of the explosion of charges of the indicated explosives on copper barriers were carried out using the Ansys Autodyn program [23].

All explosive charges were 50 mm thick and consisted of either compact or porous (2%) materials. Copper barriers in contact with charges were either a thin plate 1 mm thick or a rather thick layer 50 mm thick. For the length of the counting cell both in the charge and in the barrier, a value of 0.2 mm was chosen. The sensors for reading the calculated information were installed in an explosive charge 50 mm thick at coordinates 10, 20, 30 and 40 mm, and in a copper layer 50 mm thick at coordinates 0, 10, 20, 30 and 40 mm. In a copper plate 1 mm thick, the sensor was installed at half of its thickness. Detonation was initiated at the initial zero moment on the free surface of the charge.
Table 3. Coefficients of the JWL equation of state for compact and porous TKX-50 and explosive formulations with 5 wt% binders.

| Coefficients | TKX-50 | Paraffin | HTBP |
|--------------|--------|----------|------|
| JWL EOS      |        |          |      |
| $\rho_0$, g/cm$^3$ | 1.877  | 1.839    | 1.780| 1.744 | 1.784 | 1.748 |
| $A$, GPa     | 3064   | 2740     | 3455 | 3078  | 3520  | 2963  |
| $B$, GPa     | 79.86  | 76.68    | 82.94| 79.72 | 85.36 | 77.11 |
| $C$, GPa     | 1.485  | 1.497    | 1.360| 1.352 | 1.380 | 1.368 |
| $R_1$        | 6.540  | 6.492    | 7.021| 6.980 | 7.081 | 6.926 |
| $R_2$        | 2.058  | 2.064    | 2.172| 2.175 | 2.188 | 2.148 |
| $\omega$     | 0.508  | 0.497    | 0.526| 0.518 | 0.522 | 0.517 |
| $\mathcal{D}$, m/s | 9456   | 9282     | 9002 | 8830  | 8973  | 8805  |
| $Q$, kJ/kg   | -4711  | -4705    | -4406| -4401 | -4467 | -4460 |
| $P$, GPa     | 37.02  | 35.47    | 31.89| 30.37 | 31.83 | 30.25 |

|Coefficients | GAP | AMMO | BAMO |
|--------------|-----|------|------|
| $\rho_0$, g/cm$^3$ | 1.835 | 1.978 | 1.999 |
| $A$, GPa     | 3186 | 2794 | 2669 |
| $B$, GPa     | 82.80 | 78.47 | 76.20 |
| $C$, GPa     | 1.426 | 1.419 | 1.419 |
| $R_1$        | 6.758 | 6.680 | 6.690 |
| $R_2$        | 2.113 | 2.107 | 2.110 |
| $\omega$     | 0.541 | 0.533 | 0.532 |
| $\mathcal{D}$, m/s | 9236 | 9066 | 9121 |
| $Q$, kJ/kg   | -4655 | -4648 | -4636 |
| $P$, GPa     | 35.01 | 33.17 | 33.54 |

The coefficients of the equation of state for detonation products in the form of Jones-Wilkins-Lee (JWL EOS) for all of the explosive materials used are given in table 3. For copper, the equation of state from the Ansys Autodyn program database, denoted as CU-OHC Shock S3 EOS [24], was used. Some of the calculated results for the explosive loading of copper barriers are shown in figures 4-7. For thin plates, the character of their velocity increase is indicative, in which the general features of the process and particular moments associated with the type of explosive composition or its initial state are clearly manifested. The same is true for the displacement of the plates, where the results obtained are simply the result of the integration of velocities.

The processes associated with the formation and passage of detonation waves in charges of explosive formulations and shock waves in copper layers are more complex and interesting. Here, in the diagrams presented, only the extreme boundaries of the manifestation of these processes are marked. As in the case of plate acceleration processes, these calculations are very sensitive to the type of explosive formulation used and its initial state. In a more complete form, the results of the calculations performed and their analysis can be viewed in [25].
Figure 4 (left). Increase in the velocity of copper plates under explosion loading with compact charges of TKX-50 (above) and an explosive formulation with 5 wt.% paraffin (below).

Figure 5 (right). The maximum velocities of copper plates loaded with compact (squares) and porous (rhombuses) charges of TKX-50 and explosive formulations with 5 wt.% of specified binders: 1 - TKX-50, 2 - BAMO, 3 - GAP, 4 - AMMO, 5 - HTPB, 6 - paraffin.

Figure 6 (left). Detonation waves at coordinates 10, 20, 30, and 40 mm during explosion of compact charges of TKX-50 (above) and an explosive formulation with 5 wt% paraffin (below).

Figure 7 (right). Shock waves in a copper layer at coordinates 0, 10, 20, 30, and 40 mm when it is loaded with compact charges of TKX-50 (above) and an explosive formulation with 5 wt% paraffin (below).

3. Conclusion
Comparative calculated results on the detonation characteristics of the energetic material TKX-50, as well as of composite energetic materials based on TKX-50 with different binder contents have been obtained. Similar results were also obtained for the detonation characteristics of composite explosive formulations with 5 and 10 wt% binders and porosities of up to 10%. The use of the correct value of the standard enthalpy of formation for TKX-50 for performing thermochemical and thermodynamic calculations has been substantiated. Comparative gas-dynamic calculations of the explosive effect of TKX-50 and explosive formulations based on it on copper barriers have been carried out.
4. References

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