Short Communication

Propellants, Explosives, Pyrotechnics

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On the Question of the Energetic Performance of TKX-50

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Abstract: An analysis of the experimental data available to date shows that the explosive TKX-50 has really high explosive performance characteristics, although not as outstanding as claimed previously, due to the overestimation of the enthalpy of formation. The obtained experimental data on the dependence of the detonation velocity on the density of TKX-50 samples agree with the results of calculations, in which the experimentally determined enthalpy of formation 194.1 kJ mol^{-1} is used. The energetic performance of TKX-50 surpasses the parameters of nitramines RDX, HMX, and even CL-20, determined at the same densities. However, the calculated detonation velocity of TKX-50 at theoretical maximum density is 9287 m s^{-1}, which is slightly lower than the detonation velocity of CL-20 at maximum density. It is worth noting that the detonation velocity of the TKX-50 at the experimentally attainable density (1.8 g cm^{-3}) is 9037 m s^{-1}. Calculations using the experimentally determined enthalpy of formation show that high-energy composite propellant formulations containing TKX-50 are inferior in a specific impulse to compositions based on CL-20 and HMX.

Keywords: dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50) · enthalpy of formation · detonation velocity · energetic performance

1 Introduction

About 10 years ago, Klapotke et al. reported an innovative promising high-energy explosive dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50, Figure 1) [1]. According to published data, this substance has a calculated detonation velocity of 9698 m s^{-1} and a detonation pressure of 42.4 GPa with a maximum density of 1.877 g cm^{-3}. At that time, it possesses good thermal stability, low toxicity, and safety of handling comparable to that of RDX. In addition, calculations have predicted that TKX-50 is a better replacement of RDX in CMDB propellants [2,3]. Substitution of HMX by TKX-50 in propellants with the energetic binder (GAP/NG/BTTN) is expected to result in a four-second increase (assigned chamber pressure 7 MPa and exit pressure 0.1 MPa) in the specific impulse [2]. The outstanding parameters of the new compound have attracted the attention of researchers all over the world; in recent years, over 180 publications have been published devoted to the study of TKX-50 [4–8].

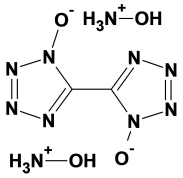

Figure 1. Structural formula of TKX-50.

2 Discussion

It is quite obvious that for a poly-nitrogenous endothermic compound with low oxygen content in the molecule, energetic performance is very strongly dependent on the enthalpy of formation. The enthalpy of formation of TKX-50 was calculated as follows. The gas phase enthalpy of formation was computed using by combining the atomization method and quantum mechanics (CBS-4M method) [9,1]. The gas phase value was converted into the solid-state enthalpy of formation by subtraction of the lattice enthalpy calculated according to Jenkins et al. [10]. The resulting enthalpy of formation of TKX-50 (446.6 kJ mol^{-1}) [1] was then shown to agree with calculated values in other works: 432 kJ mol^{-1} [11] and 396 kJ mol^{-1} [12].

However, this enthalpy of formation of TKX-50 (446.6 kJ mol^{-1}) raised doubts among the authors of reference [13]. Indeed, a simple sum of enthalpies of formation of TKX-50 constituents – hydroxylamine (−114.18 kJ mol^{-1} [14]) and 5,5′-bis(2-hydroxytetrazole) (481–531 kJ mol^{-1}, estimation based on enthalpy of formation of 5,5′-bistetrazole [15]) gives a much lower value of 253–302 kJ mol^{-1}. But it is also necessary to take into account the heat of the salt for-

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mation reaction, which is estimated to be between −100 and −150 kJ mol^{-1}. The enthalpy of formation of TKX-50 has been measured with the help of bomb calorimetry [13] and the resulting value of 111 ± 16 kJ mol^{-1} is quite different from the enthalpy reported in [1]. In [16, 17], a higher value of the enthalpy of formation (194.1 ± 0.9 kJ mol^{-1}) was obtained on a precision calorimeter, which, however, also strongly differs from the previously published one. The enthalpy of formation of TKX-50 was also calculated using classical quantum chemistry methods and an improved method of isodesmic reactions [18]. The value calculated in this article (164.1 kJ mol^{-1}) turned out to be close to the experimental values obtained in the papers [13, 16].

The energetic properties of composite propellants containing different mass fractions of TKX-50 particles were theoretically computed and experimentally evaluated in [19]. The authors found a significant discrepancy between the calculated and measured heats of an explosion, increasing as the content of TKX-50 increased. This led them to conclude that the originally published value of the enthalpy of formation of TKX-50 is highly questionable. The maximum recorded underestimation of the heat of explosion was 222 kJ per mole of added TKX-50.

Despite the published results, most of the researchers continue to use the dubious enthalpy of formation, preferring to think that they are working with the energetic compound having the detonation velocity (9698 m s^{-1}) higher than that of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20, 9455.0 m s^{-1}) at theoretical maximal density (TMD). Among the numerous studies that appeared in subsequent years, there are just a few works devoted to the experimental verification of the energetic performance of the TKX-50. Perhaps this is due to the need to synthesize a significant amount of a substance (tens and hundreds of grams) for such studies. At the same time, the authors of [20] using milligram amounts of material with help of the LASEM (laser-induced air shock from energetic materials) method estimated the detonation velocity of TKX-50 (9.56 ± 0.28 km s^{-1}), which would seem to reject doubts about the correctness of the value of the enthalpy of formation published in [1]. However, this was not a direct measurement of detonation velocity, but rather an estimation based on the measurement of the air shock produced. The correlation dependence between the shock wave velocity and the detonation velocity obtained for one type of explosives may be incorrect for a substance with a different composition of explosion products.

Recently the detonation properties of a pressed column with a diameter of 20–60 mm of TKX-50 with very little binder content (3% elastomer ETPE) were reported [21]. The results obtained were not entirely unambiguous. On the one hand, the authors showed that the determined heat of explosion of pressed TKX-50 samples is 4650 J g^{-1}, which is much lower than HMX (5599 J g^{-1} [22]). The authors explained this fact by the low oxygen balance of TKX-50. It is worth noting that the calculated heat of explosion based on the experimentally determined enthalpies of formation [13, 16] gives the value of 4250 J g^{-1} or 4590 J g^{-1}, respectively, while the use of the enthalpy of formation reported in [1] (446.6 kJ mol^{-1}) leads to a predicted values of (5610 J g^{-1}), which is significantly higher than the experimental value.

On the other hand, the resulting dependence of the detonation velocity on density in the range 1.555–1.740 g cm^{-3}, allowed the authors [21] to assume that the detonation velocity of TKX-50 at theoretical maximum density might be 9432 m s^{-1}, which is higher than the detonation velocities of RDX (8800 m s^{-1}) and HMX (9150 m s^{-1}) at their respective TMDs.

A closer examination of the data obtained in [21] (Figure 2) shows that using the obtained dependence of detonation velocity on density for extrapolation calculations is not entirely correct. First, the drop in the detonation velocity with a decrease in density below 1.7 g cm^{-3} is stronger than theoretical calculations (lines in Figure 2) suggest. Second, the authors of [21] did not take into account the point in this dependence at a density of 1.8 g cm^{-3} and the same charge diameter (30 mm). Taking this point into account, the dependence acquires a nonlinear character (Figure 2), which does not allow the construction of an extrapolation dependence.

The authors of [21] found that when the charge diameter changes from 20 to 60 mm (density 1.8 g cm^{-3}), the detonation velocity increases by more than 300 m s^{-1} (from 8700 to 9037 m s^{-1}). This means that the diameter of 20–30 mm at a density of 1.8 g cm^{-3} is less than the "limiting"

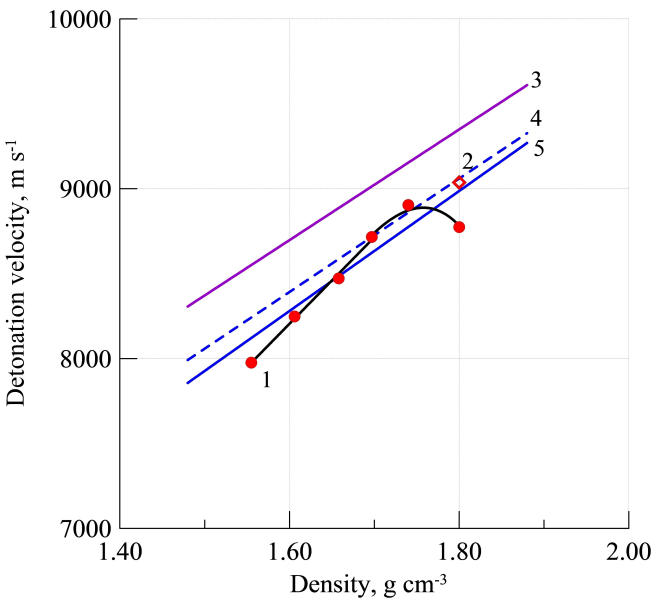

Figure 2. Comparison of TKX-50 experimental data (1- sample diameter 30 mm, 2- sample diameter 60 mm) and calculated detonation velocity dependences on sample density (3 – $\Delta H_f^0 =$ 446.6 kJ mol^{-1} [1], 4 – $\Delta H_f^0 = 194.1$ kJ mol^{-1} [16], 5 – $\Delta H_f^0 =$ 111 kJ mol^{-1} [13]).

diameter, from which the detonation velocity ceases to depend on the diameter. This is due to the fact that the critical, and, accordingly, the limiting detonation diameters sharply increase as the charge density approaches the maximal one. The reason for this phenomenon lies in the change in the detonation initiation mechanism from focal to homogeneous with an increase in the explosive density. In the latter case, the size of the reaction zone increases sharply, and, accordingly, the critical and limiting diameters grow.

Thus, on going from a density of 1.0 to 1.8 g cm^{-3}, the critical diameter of RDX increases from 1 to 7 mm, and for HMX even up to 18 mm (density 1.9 g cm^{-3}) [23]. According to the gap test performed in [21], the high-nitrogen compound TKX-50 has a critical initiation pressure much higher than HMX; therefore, it can be assumed that TKX-50 has a significantly larger critical diameter of detonation than HMX.

Consequently, the nonlinear character of the D(ρ) dependence at a charge diameter of 30 mm is due to the extreme nature of the dependence of the critical diameter on the density, which passes through a minimum in this density range.

For comparison, Figure 2 shows the calculated dependences of the detonation velocities vs. densities. All calculations of detonation velocity at different sample density were carried out with the thermochemical equilibrium code Shock & Detonation [24], based on the original equation of state [25].

Note that the experimental detonation velocities of TKX-50 are grouped near the calculated dependences D(ρ), in which the enthalpies of formation obtained in [13,16] were used, but significantly lower than the dependence D(ρ) calculated with the enthalpy given in [1] (Figure 2).

It can be assumed that the normal detonation process of pressed TKX-50 charges is observed in the range of densities 1.70–1.74 g cm^{-3} for a diameter of 30 mm, and for a density of 1.8 g cm^{-3} only at a diameter of 60 mm. These experimental points are described by the dependence D (m s^{-1}) = 3059 ρ + 3545, the slope of which is consistent with the slope of the calculated dependences, and the points themselves practically coincide with the calculated dependence at the enthalpy of formation of 194.1 kJ mol^{-1} obtained in [16] (Figure 3). For comparison, Figure 3 shows

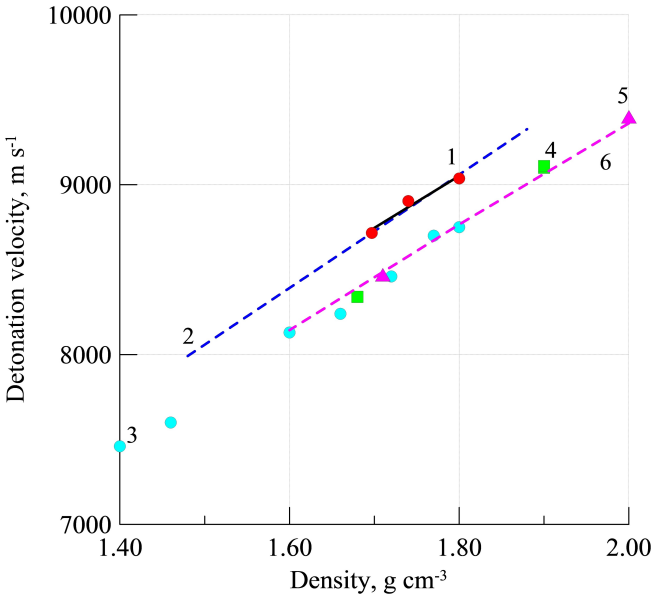

Figure 3. Comparison of TKX-50 experimental data (1), calculated detonation velocity (2 – ΔH_f^0 = 194.1 kJ mol^{-1}) and experimental detonation velocity of RDX(3), HMX (4) and CL-20(5) at different densities. Dashed line 6 is calculated data for CL-20.

the experimental detonation velocities of common explosive RDX, HMX, and CL-20 [26].

As can be seen from the Figure 3, the energetic performance of TKX-50 really surpasses the parameters of nitramines RDX, HMX, and even CL-20, determined at the same densities [26]. However, the detonation velocity of TKX-50 at TMD according to the above dependence is 9287 m s^{-1}, which is slightly lower than the detonation velocity of CL-20 at maximum density.

It could be expected that the observed advantage of the high-nitrogen compound TKX-50 over nitramines is due to the higher specific enthalpy contribution to the heat of the explosion. However, this is not the case. As can be seen from Table 1, the contribution from the heat of formation of TKX-50 exceeds the similar contribution of nitramines RDX and HMX, but does not exceed those for CL-20.

Moreover, TKX-50 is inferior to all three nitramines in terms of the calculated heat of the explosion, and CL-20 has

Table 1. Comparative thermodynamic calculations for TKX-50 and some common nitramines.

Compounds	ΔH^0_f,[a] kJ kg^{-1}	$D_{max}(\rho)$,[b] m s^{-1} (g cm^{-3})	Q_{ex},[c] kJ kg^{-1}	V,[d] l kg^{-1}
RDX	316.5	8750 (1.8)	6196	762
HMX	295.3	9110 (1.9)	6149	761
CL-20	861.3	9400 (2.0)	6468	707
TKX-50	822.5 [16]	9037 (1.8)	4874	847

[a] Enthalpy of formation [27]. [b] Maximum measured detonation velocity (density). [c] The estimated heat of explosion. [d] The volume of explosion products.

the highest heat of the explosion. However, during the explosion of CL-20, the least amount of gaseous products is released, while TKX-50 surpasses all the given nitramines in this parameter.

Let us now consider how the value of the enthalpy of formation of TKX-50 affects its efficiency as a component of rocket propellants. As noted earlier, substitution of HMX by TKX-50 in propellants with the energetic binder is expected to result in a four-second increase in the specific impulse [2]. A similar result was predicted for TKX-50-based solid rocket propellant formulation (22% energetic binder, 20% oxidizer, 18% Al, 40% TKX-50) [28] and for propellant with GAP/NG energetic binder [4]. However, the motor test of HTPB propellant with TKX-50 shows that the specific impulse is lower than that of RDX-based reference [29]. The authors concluded that the lower enthalpy of formation of the TKX-50 (about 210 kJ/mol) is the main reason that leads to the lower energy content.

Our calculations using the experimentally determined enthalpy of formation (194.1 $kJ\,mol^{-1}$) show that high-energy composite (HEC) propellant formulations suggested in [4] containing TKX-50 have a lower specific impulse in comparison to HEC, based on CL-20 and even HMX (Table 2). Theoretical rocket performances were calculated with thermochemical equilibrium code REAL [30], taking the assigned pressure ratio (p_c/p_e) to be 70 (assigned chamber pressure 7 MPa and exit pressure 0.1 MPa). The calculation is performed assuming equilibrium flow conditions.

As can be seen from Table 2, the value of the enthalpy of formation of the additive plays an important role in the energetic characteristics of the HEC propellants.

Table 2. Calculation results of specific impulse for various HEC propellant formulations.

High-energy explosive component	HMX	CL-20	TKX-50
Formulation	10% GAP, 15% NG, 18% Al, 45% HMX, 12% AP	10% GAP, 15% NG, 18% Al, 54% CL-20, 3% AP	10% GAP, 15% NG, 18% Al, 41% TKX-50, 16% AP
Oxygen balance [%]	−33	−33	−33
Specific impulse [s]	274[a] 274[b]	275[a] 274.5[b]	278[a] 277.5[b] **271.4**[c]

[a] Calculation [4] with the thermochemical equilibrium code EXPLO5 (TKX-50 $\Delta H^0_f = 446.6$ kJ/mol). [b] Calculation (this work, for comparison) with the thermochemical equilibrium code REAL [30] (TKX-50 $\Delta H^0_f = 446.6$ kJ/mol). [c] Calculation (this work) with the thermochemical equilibrium code REAL [30] (TKX-50 $\Delta H^0_f =$ 194.1 kJ/mol).

3 Conclusion

An analysis of the experimental data available to date shows that the explosive TKX-50 has really high explosive performance characteristics, although not as outstanding as claimed previously, due to the overestimation of the enthalpy of formation. The obtained experimental data on the dependence of the detonation velocity on the density of TKX-50 samples with a diameter of 30–60 mm agree with the results of calculations, in which the enthalpy of formation (194.1 $kJ\,mol^{-1}$) experimentally determined in [16] is used. This value is significantly less than the originally reported value. It is worth noting that the detonation velocity of the TKX-50 at the experimentally attainable density (1.8 $g\,cm^{-3}$) is 9037 $m\,s^{-1}$. However, the TKX-50 is significantly less sensitive to external influences than the HMX and CL-20, which shows big potential for future application as a secondary explosive.

Concerning potential of TKX-50 for application in rocket and gun propellants, calculations using the experimentally determined enthalpy of formation show that high-energy composite propellant formulations containing this component are inferior in a specific impulse to compositions based on CL-20 and HMX. Since the density of TKX-50 (1.877 $g\,cm^{-3}$) is less than that of HMX (1.906 $g\,cm^{-3}$) and ε-CL-20 (2.04 $g\,cm^{-3}$), therefore, one should not expect a higher value of density impulse for compositions with TKX-50, compared to similar formulations containing CL-20 and HMX.

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Data Availability Statement

Data openly available in a public repository that issues datasets with DOIs.

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