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Experimental Study on the Heat Resistant Explosive 5,5'-Bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole) (TKX-55): the Jet Penetration Capability and Underwater Explosion Performance^{*}

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Abstract: Ongoing research to find new explosives which are stable at high temperatures focuses on compounds which comply with the strict requirements which must be fulfilled in order for a compound to be of use in deep oil-well and gas drilling applications. Great efforts have been focused on the development of new, thermally stable explosives which are stable at even higher temperatures than hexanitrostilbene, and which also show superior performance. In the group of recently synthesized thermally stable explosives, 5,5'-bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole) (TKX-55) is one of the most promising prospective candidates for use in practical applications, due to its physicochemical properties as well as its convenient synthesis. Therefore, further investigation into the performance of TKX-55 in shaped charge applications was undertaken. This study was focused on the investigation of the jet penetration capability of conical shaped charges filled with TKX-55, in comparison with recently used other explosives. The kinetic energy of the jet depends on the brisance of the explosive which is used. In order to experimentally investigate the shattering effect of TKX-55, the Underwater Explosion Test was applied. Based on the collected data, the total energy, as the sum of the primary shock wave energy (the brisance) and the bubble gas energy (the heaving effect), was calculated.

Keywords: thermally stable explosive, TKX-55, shaped charge, underwater detonation

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1 Introduction

Research on thermally stable explosives is conducted in many research groups worldwide [1-8]. However, there are strict demands which thermally stable explosives must meet: tailored performance, sensitivity, stability, vulnerability, environmental safety, low solubility in water, longevity and compatibility. Explosives which are stable at high temperatures and low pressures are used in perforating charges in the mining industry to obtain oil and gas from wells. Perforation with shaped charges is currently a common method of achieving a connection between the deposit and the geological borehole. It is also used for uncovering other deposits, such as mineral water, geothermal sources, shell gas, sulfur resources, as the most cost-effective method [9]. In this area of research, the following explosives have received particular interest: 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [10-17], 2,2',4,4',6,6'-hexanitrostilbene (HNS) [16-24] and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) [25-29]. Other interesting heat resistant explosives such as 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl (NONA) and 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) [30-32], (Figure 1) are currently under investigation.

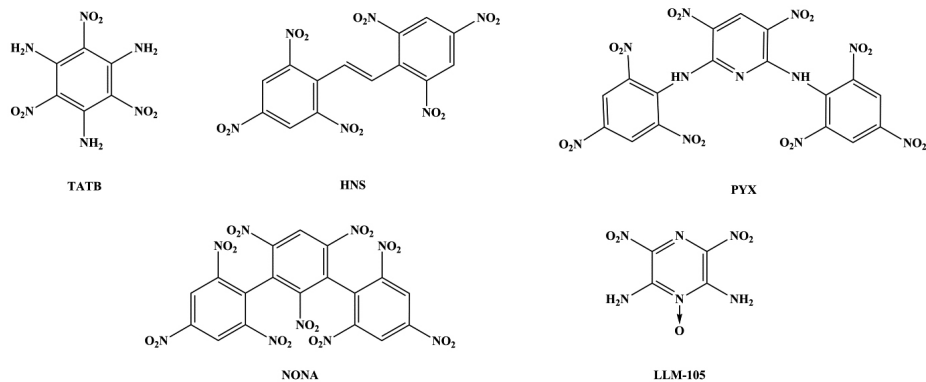
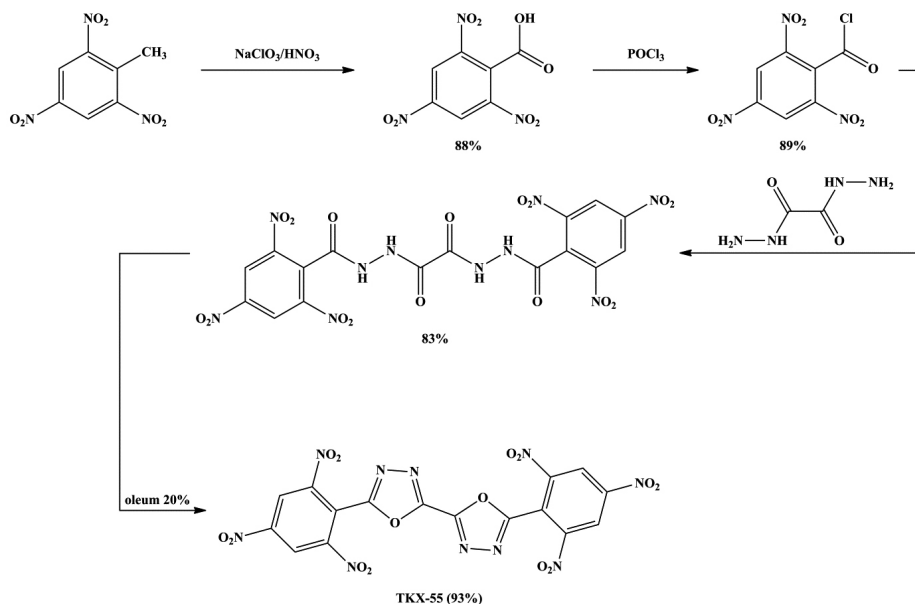


Figure 1. 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB), 2,2',4,4',6,6'-hexanitrostilbene (HNS), 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX), 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl (NONA) and 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105).

Many research groups are currently trying to find new heat resistant explosives which show lower sensitivity and better performance than HNS. Among the recently reported heat resistant explosives, 5,5'-bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole) (TKX-55) is one of the most promising

candidates for application, because of its good physicochemical properties as well as its convenient synthesis (Scheme 1) [33].



Scheme 1. Synthesis of 5,5'-bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole) (TKX-55) [33].

TKX-55 is a covalent species consisting of a conjugated system with six nitro explosophore functionalities attached to it. Moreover, the inclusion of the endothermic 1,3,4-oxadiazole heterocyclic moieties into the conjugated system increases the heat of formation of the final compound. The calculated standard molar enthalpy of formation for TKX-55 ($197.6 \text{ kJ}\cdot\text{mol}^{-1}$) is more than 2.5 times higher than that of HNS, and more than 4.5 times higher than that of PYX (78.2 and $43.7 \text{ kJ}\cdot\text{mol}^{-1}$, respectively) [33]. The measured density of TKX-55 is $1.837 \text{ g}\cdot\text{cm}^{-3}$ (pycnometer measurement at 298 K) which is higher than the reported densities of HNS and PYX [33]. The high density, as well as the high value for the heat of formation, are the reasons for the high detonation parameters of TKX-55 (computed using the EXPLO5 V6.01 thermochemical computer code) [34]: detonation velocity ($V_{C-J} = 8030 \text{ m}\cdot\text{s}^{-1}$) and detonation pressure ($p_{C-J} = 27.3 \text{ GPa}$) [33]. The thermal stability of TKX-55 is high, with decomposition at $335 \text{ }^\circ\text{C}$ (onset value) determined using differential scanning calorimetry (DSC, $\beta = 5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$) [33]. The friction sensitivity of TKX-55 is lower ($>360 \text{ N}$) than the measuring range of the friction testing apparatus. The

impact sensitivity of TKX-55 is 5 J, which is equal to the value reported for HNS. TKX-55 is also less sensitive toward electrostatic discharge than PYX and HNS [8, 33]. Since the properties of TKX-55 are remarkable in comparison with those of HNS and PYX, we decided to perform further investigations into TKX-55.

This study focused on an investigation of both the effective perforation of conical shaped charges filled with the new thermally stable explosive (TKX-55), and the initiating capability of detonators containing TKX-55 as a base charge (applying the Underwater Explosion Test).

2 The Jet Penetration Capability

In order to study the jet penetration capability of shaped charges containing TKX-55 as a base charge, the methodology described in the standard PN-C-86045:1997, was applied [35]. The essential impact on the depth of the jet penetration have the symmetry and homogeneity of the liner. In order to meet all of the requirements which are desired for the geometry and structure of the liners, powder metallurgy technology was applied [9, 36-38]. Liners were manufactured by compression molding of electrolytic copper powder (ECu, the diameter of the spherical copper grains was approximately 10 μm), followed by low temperature sintering of the liners in an inert atmosphere. The symmetry and homogeneity of the powder liners were assessed on a spinning table workstation and by measuring the liners' wall thickness at predetermined measurement points [9]. The liners which were obtained had the following characteristics: outer diameter (34.70 ± 0.01 mm), apex angle ($60.00 \pm 0.01^\circ$), mass (18.00031 ± 0.00002 g), and density (8.40 ± 0.01 g·cm⁻³) – Figure 2.



Figure 2. Liners made from copper (ECu) powder.

Further factors which have a significant impact on the jet penetration capability are the physicochemical properties of the explosive that is used as the main charge. In our experiments, TKX-55 was investigated and the results compared with those obtained using RDX and RDX phlegmatized with 1.5% polyfluoroethylene [33, 39]. The mass of the base charge which was used for each shaped charge was constant

(16.00 ± 0.01 g). The explosive plus liner were press-molded into a steel case at ambient temperature under a pressure of 215 MPa. For each explosive, five shaped charges were prepared. The densities for TKX-55, RDX, and RDX + 1.5% PTFE charges which were obtained were equal to: 1.43, 1.46, and $1.51 \text{ g}\cdot\text{cm}^{-3}$, respectively. An example of the shaped charge which was used for assessing the jet penetration capability and a schematic drawing are shown in Figure 3.

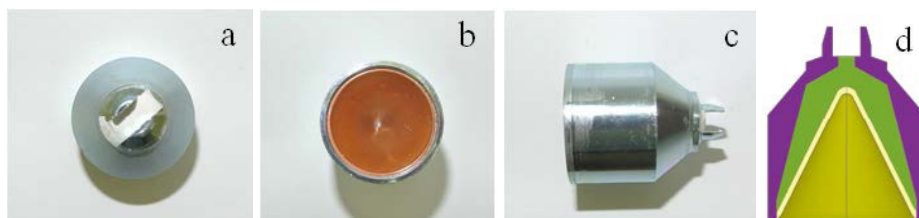


Figure 3. Views of a shape charge filled with 16.00 g of TKX-55 (a-c), and a schematic drawing of the shaped charges which were used in this work (d).

The shaped charges which were under investigation, were placed at a standoff distance equal to 1.5 caliber of the liner, above a stack of steel plates (steel grade St3, thickness 10.00 ± 0.01 mm). The shaped charges were connected using an RDX detonating cord in a lead case with a commercially available detonator (NITROERG – ERGODET 0.2 A). The test arrangement for the firing of the shaped charges is shown in Figure 4.



Figure 4. The test arrangement for firing the shaped charge: view of the shaped charge filled with TKX-55 placed at the standoff distance on the stack of witness plates (left) and the complete arrangement for the test (right).

After the shaped charges had been fired, the depth of penetration (h), inlet diameter (φ_i) and volume of the crater (V) were determined (Table 1). The results of the action of the shaped charge filled with TKX-55 as a base charge is shown in Figure 5.

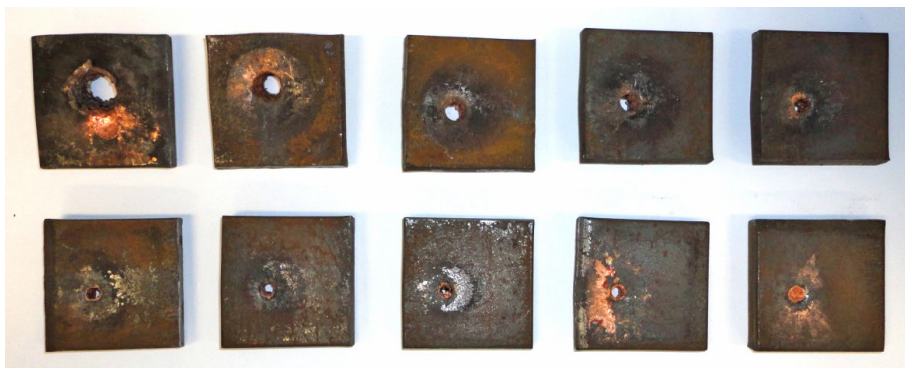


Figure 5. Steel witness plates after firing of the shaped charge filled with TKX-55.

Table 1. Values of h , φ_i , and V obtained for the investigated shaped charges

Explosive	h [mm]	φ_i [mm]	V [mm ³]
RDX	127.3 (1.9)	14.1 (2.4)	5800 (2.9)
RDX + 1.5% PTFE	124.1 (2.2)	11.3 (2.6)	5500 (3.3)
TKX-55	91.2 (1.8)	13.4 (2.7)	3200 (3.0)

Coefficient of variation (CV, %) is given in parentheses.

The largest values for the depth of penetration, inlet diameter and volume of the crater were obtained when RDX was used. The introduction of 1.5% PTFE resulted in a decrease in h , φ_i , and V in comparison to RDX (97.49, 80.14, and 94.83% of RDX values respectively). TKX-55 gave smaller h , φ_i , and V values than RDX (71.64, 95.04, and 55.17% of RDX values, respectively).

3 The Initiating Capability of Detonators

In order to determine the initiating capability of detonators containing TKX-55 and PYX as a base charge, the underwater explosion test was used [40-46]. The investigated explosives (0.2 g, 0.5 g and 0.7 g) were pressed into aluminum shells under a pressure of 4.40 MPa. Each of the tests using the explosive samples were carried out five times. For the 0.5 g and 0.7 g base charge masses, two identical loading operations were undertaken (2×0.25 g and 2×0.35 g, respectively). The priming charge (lead azide, 300 mg) was compressed at 4.40 MPa into an inner cup, and placed onto the base charge by applying a pressure of 4.40 MPa. Afterwards, an electric fuse-head with a sealing plug and leading wires was fixed to the loaded detonator shell and an inner cup filled with lead azide. In order to carry out the underwater explosion tests, a water tank was constructed from energy-absorbing and non-reflecting material, with a positioning system for the sensor and detonator (Figure 6).



Figure 6. The arrangement for the underwater explosion tests (left) and the positioning system with the sensor and detonator (right).

A voltage mode tourmaline pressure sensor (PCB Piezotronics, Inc, model 138A05) and oscilloscope (Agilent, model 54622A) were used to collect the data. The testing conditions during measurements were constant and as follows: water temperature 11 °C, atmospheric pressure 982 hPa. The overpressures which were generated in the water were recorded by a piezoelectric transducer. Subsequently, the collected data ($I = f(t)$) by using the characteristics of the pressure sensor was transferred into $P = f(t)$ relationship. The characteristics of the primary shock wave generated in water were used to determine the maximum of the overpressure (P_{max}), and the time at which the sensor output had decreased to $P_{\theta} = P_{max} \cdot e^{-1}$ (θ), and to calculate the primary shock-wave energy (E_{SW}) and the shock energy equivalent (E_S) (Figure 7, Tables 2 and 3).

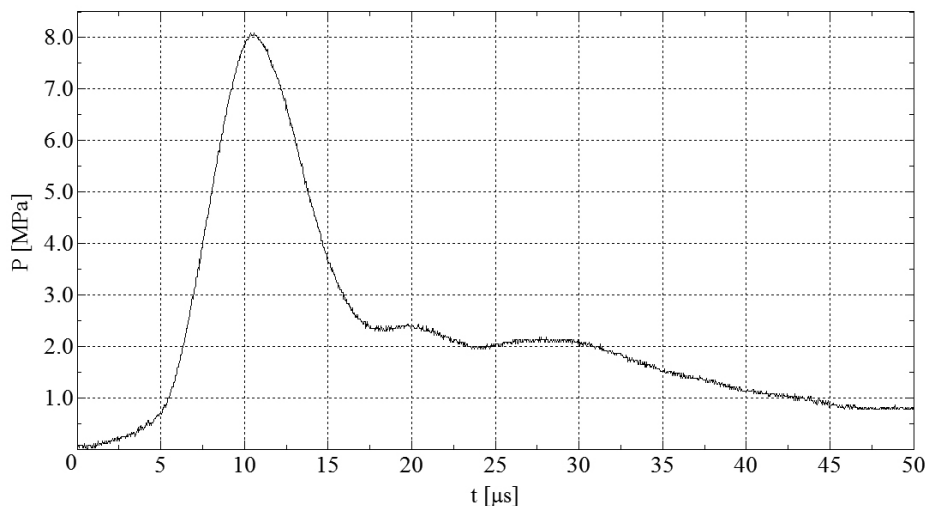


Figure 7. The primary shock wave generated in water by firing a detonator filled with 0.7 g TKX-55 as the base charge.

Using the data which was obtained, the time interval between the shock-wave pressure peak and the first collapse of the gas bubble (t_b) was determined, and the bubble gas energy (E_{BW}), and bubble energy equivalent (E_B) were calculated (Figure 8, Tables 2 and 3).

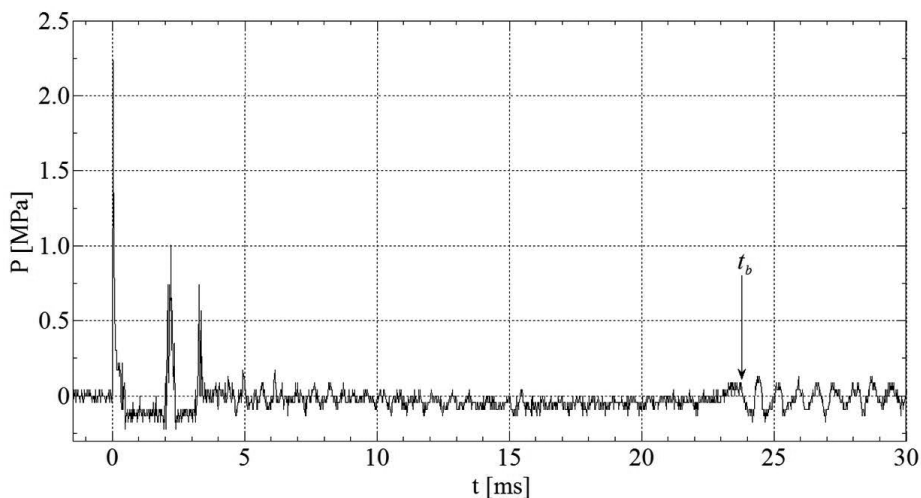


Figure 8. Overpressure generated in water by firing a detonator containing 0.7 g TKX-55 as the base charge.

The total energy (E) generated in water by PYX and TKX-55 (0.2 g, 0.5 g, 0.7 g) is summarized as a graph in Figure 9.

Table 2. Values of the experimental shock wave parameters P_{max} , P_{θ} , Θ and t_b for PYX and TKX-55

Explosive	m [g]	ρ [g·cm ⁻³]	P_{max} [MPa]	P_{θ} [MPa]	Θ [μs]	t_b [ms]
PYX	0.20 (0.28)	1.05 (0.34)	5.45 (3.54)	2.01	16.52 (2.70)	16.35 (0.83)
	0.50 (0.57)	1.40 (0.63)	7.41 (0.74)	2.73	16.46 (0.77)	22.07 (0.45)
	0.70 (0.18)	1.42 (0.57)	8.41 (1.37)	3.09	16.16 (3.31)	23.88 (0.49)
TKX-55	0.20 (0.36)	1.25 (0.40)	5.38 (0.73)	1.98	13.79 (1.76)	18.21 (0.28)
	0.50 (0.33)	1.18 (0.39)	7.09 (0.97)	2.61	15.14 (1.95)	22.10 (0.69)
	0.70 (0.17)	1.17 (0.39)	8.25 (0.76)	3.04	16.34 (1.37)	24.09 (0.48)

Coefficient of variation (C_V , %) is given in parentheses.

Table 3. Values of the calculated shock wave parameters E_S , E_{SW} , E_B , E_{BW} , and E for PYX and TKX-55

Explosive	m [g]	$E_S \cdot 10^8$ [Pa ² ·s]	E_{SW} [J]	$E_B \cdot 10^{-6}$ [s ³]	E_{BW} [J]	E [J]
PYX	0.20	1.46	198.27	4.37	339.85	538.12
	0.50	2.84	385.68	10.75	835.88	1221.56
	0.70	3.67	498.39	13.62	1058.87	1557.26
TKX-55	0.20	1.45	196.91	6.04	469.54	666.45
	0.50	2.60	353.08	10.79	839.30	1192.38
	0.70	3.46	469.87	13.98	1087.05	1556.92

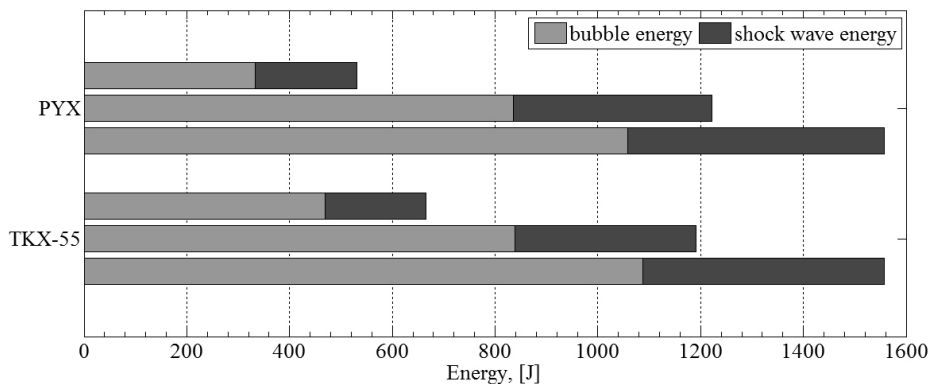


Figure 9. Total energies (E) generated in water by PYX and TKX-55 (0.2 g, 0.5 g, 0.7 g).

The densities obtained during the experiments were lower than the maximum determined densities. These differences in the densities are due to the methodology which was used, which is described in the European Standard [42], *i.e.* the same pressing pressure (4.40 MPa) for the investigated explosives. The lowest density for PYX was obtained for base charges of 0.2 g. In the case of TKX-55 the opposite was observed. This has a direct impact on the experimental shock wave parameters (P_{max} , P_{Θ} , Θ , t_b), as well as the values for E_S , E_{SW} , E_B , E_{BW} , E , which were calculated using the experimental shock wave parameters. Nevertheless, the value of the pressing pressure was kept constant for comparative reasons. Additionally, the underwater test results were supported by the calculated detonation parameters at the recorded densities. The values of the peak overpressure of TKX-55 were slightly lower than those registered for PYX. The time required for the decrease in the overpressure to $P_{max} \cdot e^{-1}$ are comparable for TKX-55 and PYX. These two factors confirm that the primary shock waves (and thus brisance) generated by TKX-55 and PYX are similar. Moreover, the first bubble collapse registered for TKX-55 and PYX are also comparable. This indicates similar action (heaving power) for TKX-55 and PYX at larger distances from the point of initiation. Finally, the calculated total energies, as the sum of the primary shock wave energy and the bubble gas energy of TKX-55 (for 0.5 g and 0.7 g base charges), are similar to those obtained for PYX, while for the 0.2 g base charges, TKX-55 generates a larger amount of bubble energy and therefore the total energy released by TKX-55 is higher than that of the total energy of PYX.

4 Detonation Parameters

The gas-phase absolute molar enthalpies at 298 K and 1 atm were calculated theoretically using the modified complete basis set method (CBS-4M; M referring to the use of minimal population localization) with the Gaussian 09 software [47-49]. Gas-phase standard molar enthalpies of formation ($\Delta H_f^\circ(g)$) at 298 K were computed using the atomization energy method [50-53]. Standard molar enthalpies of formation were calculated using $\Delta H_f^\circ(g)$ and the standard molar enthalpies of sublimation by applying Trouton's rule [54-55]. The Chapman-Jouguet (C-J) characteristics, (*i.e.* detonation temperature, T_{C-J} ; detonation pressure, p_{C-J} ; detonation velocity V_{C-J}) based on the calculated standard molar enthalpy of formation values (PYX: 43.7, HNS: 78.2, TKX-55: 197.6 kJ·mol⁻¹) and the densities were performed with the CHEETAH (version 2.0) thermochemical code [33, 56]. The calculations for the explosives assume ideal behaviour. The Becker-Kistiakowsky-Wilson equation of state (BKW EOS) for gaseous detonation products with the BKWC product library and the BKWC set of parameters ($\alpha=0.49912$, $\beta=0.40266$, $\kappa=10.864$, $\Theta=5441.8$) were used in the calculations. The total detonation energy (E_0) as the sum of the mechanical and thermal energies was calculated assuming frozen expansion of the detonation products at 2145 K (Table 4).

Table 4. Calculated values of T_{C-J} , p_{C-J} , V_{C-J} and E_0 for PYX, HNS and TKX-55

	ρ [g·cm ⁻³]	$\rho \cdot \rho_{TMD}^{-1}$ [%]	$T_{C-J}^{a)}$ [K]	$p_{C-J}^{b)}$ [GPa]	$V_{C-J}^{c)}$ [m·s ⁻¹]	$-E_0^{d)}$ [kJ·cm ⁻³]
PYX	1.757	100.00	3974	24.44	7462	8.215
	1.42	80.82	3970	15.04	6463	6.075
	1.40	79.68	3965	14.59	6404	5.956
	1.05	59.76	3829	8.13	5385	4.032
HNS	1.74	100.00	4048	23.24	7227	8.406
TKX55	1.837	100.00	4059	27.02	7630	8.684
	1.25	68.05	4004	11.45	5948	5.049
	1.18	64.24	3972	10.17	5747	4.673
	1.17	63.69	3967	10.00	5718	4.620

^{a)} Detonation temperature; ^{b)} detonation pressure; ^{c)} detonation velocity; ^{d)} detonation energy.

The calculated detonation parameters (for the maximum density of the explosive charges) using the CHEETAH (version 2.0) code, differed from those obtained using EXPLO5 (version 6.01). The largest differences were found for

the detonation temperature, with the CHEETAH values being much higher than those obtained using EXPLO5. Nevertheless, the calculated values have the same tendency [33]. TKX-55 was calculated as showing a higher detonation temperature, detonation pressure, detonation velocity, and detonation energy than PYX or HNS.

5 Synthesis

TKX-55 and PYX were synthesized according to the methods given in the literature [27, 28, 33]. All compounds were isolated and characterized using multinuclear (^1H , ^{13}C) NMR and elemental analysis. The NMR spectra were recorded with a JEOL Eclipse 400 ECX instrument. Elemental analyses were carried out in the Department's internal micro analytical laboratory on an Elementar Vario EL by pyrolysis of the sample and subsequent analysis of the gases formed. Industrially produced explosives were supplied by Chemical Works "NITRO-CHEM" S.A.

TKX-55

Bis(2,4,6-trinitrobenzoyl)oxalohydrazide [33]

Oxalyldihydrazide (5 mmol, 0.59 g) was added in one portion to a solution of 2,4,6-trinitrobenzoyl chloride (10 mmol, 2.76 g) in tetrahydrofuran (THF, 25 mL). The mixture was stirred for 72 h at ambient temperature. The precipitate was filtered off and washed with THF, acetone, and diethyl ether (yield 2.48 g, 83%). ^1H NMR (400.18 MHz, DMSO- d_6 , 25 °C, ppm) δ : 11.47 (s, 2H, NH), 11.42 (s, 2H, NH); 9.13 (s, 4H, CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.0 MHz, DMSO- d_6 , 25 °C, ppm) δ : 158.0, 157.5, 147.92, 147.91, 129.2, 124.1; EA (C₁₆H₈N₁₀O₁₆, 596.29): calc.: C 32.23, H 1.35, N 23.49 (%); found: C 32.22, H 1.61, N 22.87 (%).

5,5'-Bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole), TKX-55 [33]

Bis(2,4,6-trinitrobenzoyl)oxalohydrazide (1 mmol, 0.60 g) was added to fuming sulfuric acid (20%, 10 mL). The mixture was stirred for 24 hours at ambient temperature before being poured onto crushed ice. The precipitate which formed was filtered off and washed with water until it was acid free, and was subsequently dried (yield 0.52 g, 93%). ^1H NMR (400.18 MHz, DMSO- d_6 , 25 °C, ppm) δ : 9.40 (s, 4H, CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.0 MHz, DMSO- d_6 , 25 °C, ppm) δ : 158.1, 154.0, 150.3, 149.4, 125.3, 116.8; EA (C₁₆H₄N₁₀O₁₄, 560.26): calc.: C 34.30, H 0.72, N 25.00 (%); found: C 34.33, H 1.01, N 25.01 (%).

PYX

2,6-Bis(picrylamino)pyridine (Pre-PYX) [28]

Magnesium hydroxide (1.05 g, 18 mmol) and 2,6-diaminopyridine (0.98 g, 9 mmol) were added to a solution of picryl chloride (4.95 g, 20 mmol) in *p*-xylene (40 mL). The reaction mixture was heated at 140 °C for 3 h and then allowed to cool to room temperature. Toluene (30 mL) was then added and the product was collected by filtration, washed with methanol, 10% HCl and with water until it was acid free. Yield: 62%, 2.97 g. $^1\text{H NMR}$ (400.18 MHz, DMSO- d_6 , 25 °C, ppm) δ : 10.37 (s, 2H, NH), 8.77 (s, 4H, CH), 7.75 (t, 1H, $J=8.02$ Hz, CH), 7.75 (d, 2H, $J=8.02$ Hz, CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.0 MHz, DMSO- d_6 , 25 °C, ppm) δ : 154.7, 143.1, 139.4, 139.1, 136.7, 125.7, 99.2; EA (C₁₇H₉N₉O₁₂, 531.31): calc.: C 38.43, H 1.71, N 23.73 (%); found: C 38.29, H 1.88, N 23.57 (%).

2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX) [27]

2,6-Bis(picrylamino)pyridine (1.06 g, 2 mmol) was carefully added to fuming nitric stirred acid (11 mL) at -20 °C. The resulting solution was allowed to warm to room temperature, stirred for 2 h, then heated under reflux for 5 h before being cooled and diluted with 65% nitric acid (21 mL) at 0 °C. The precipitated product was filtered off, washed with 70% nitric acid (3 mL), water until HNO₃ free, and finally with methanol (21 mL). The product which was obtained was dried at 150 °C. Yield: 67%, 0.83 g. $^1\text{H NMR}$ (400.18 MHz, DMSO- d_6 , 25 °C, ppm) δ : 11.25 (s, 2H, NH), 9.19 (s, 1H, CH), 8.90 (s, 4H, CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.0 MHz, DMSO- d_6 , 25 °C, ppm) δ : 161.2, 144.4, 142.3, 137.7, 131.2, 125.1, 124.0; EA (C₁₇H₇N₁₁O₁₆, 621.30): calc.: C 32.86, H 1.14, N 24.80 (%); found: C 32.68, H 1.38, N 24.29 (%).

6 Conclusions

TKX-55 shows excellent properties (V_{C-P} , p_{C-P} , E_0 , FS , IS , ESD and temperature of decomposition) and an easy and straightforward method of synthesis, which makes TKX-55 remarkable in comparison to HNS and PYX. The jet penetration capability of TKX-55 is much lower than that of RDX, however, RDX would be inadequate as an explosive which must be stable at very high temperatures since it decomposes at temperatures as low as 210 °C. For a better comparison of the jet penetration capability, shaped charges containing PYX and HNS as the base charge should be performed. The primary shock waves (and thus brisance) generated by TKX-55 and PYX are similar. The first bubble collapse obtained for

TKX-55 and PYX are also comparable. This indicates a similar action (heaving power) of TKX-55 and PYX at larger distances from the point of initiation.

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