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New Secondary Explosives and Oxidizers: TKX-50 and TNEF

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Abstract

The energetic materials research group at LMU has been interested in the synthesis and energetic properties of new explosives and rocket propellant ingredients for many years. Out of the many interesting compounds which we have prepared over the years, the most promising candidate compound for use in real-life applications is the secondary explosive TKX-50. An overview of the synthesis and properties of TKX-50 will be given, as well as recent aspects we have investigated. The progress and development of new CHNO-based oxidizers will also be discussed, focusing predominantly on 2,2,2-trinitroethyl formate (tris(2,2,2-trinitroethyl)orthoformate, TNEF).

Keywords: *Secondary explosives, oxidizers, TKX-50, BTNEO, TNEF*

1. Introduction

Within the area of secondary explosives, the major topics and challenges of today are to find compounds which can be prepared on an industrial scale for use as secondary explosives which have – in addition to the standard properties every secondary explosive must possess – (i) higher performance than current state-of-the-art secondary explosives, (ii) higher insensitivity (i.e. lower sensitivity) to external stimuli such as impact, friction or electrostatics and (iii) lower toxicity and higher environmental compatibility.

If these goals are considered in more detail, it is clear that a higher performance is always advantageous. Higher performance means that the secondary explosive shows higher values for detonation velocity, detonation pressure and heat of detonation. In particular, for new secondary explosives, it is important to increase performance specifically in the areas of blast effect (for destructive effect), metal acceleration, and with respect to shaped charges. In the field of secondary explosives, performance is closely associated with the following parameters, all of which can be predicted using the EXPLO5 [https://www.ozm.cz/explosives-performance-tests/thermochemical-computer-code-explo5/] thermochemical computer code [1], or measured experimentally: (i) detonation velocity ("velocity of detonation," VoD in ms^{-1}), (ii) detonation pressure ("Chapman-Jouguet pressure," p_{C-J} in GPa) and (iii) detonation heat (Qex in $kJkg^{-1}$) ([2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15]). The large samples required and difficulties in measuring parameters such as VoD and p_{C-J} experimentally mean that the energetic performance parameters of new secondary explosives are always calculated in the first instance, and only the most promising candidate compounds are prepared on a larger scale for testing.

Reduced sensitivity is an aspect which is particularly important in the areas of mechanical sensitivity (bullet impact), greater thermal stability (fuel fires), and tandem-shaped charges (two shaped charges placed in sequence). In each of these areas, the aim is to prevent unintended and unwanted detonation of a secondary explosive due to initiation caused by sensitivity of the secondary explosive to an external stimulus such as impact or heat. This is vital in improving safety, and also in widening the work-range a secondary explosive can be used in. Reduced toxicity and lower environmental impact refer not only to the explosive itself, but also to its detonation products, as well as its degradation products in the environment. In addition, reduced toxicity can also be applied to the production of the explosive which should not involve any toxic chemicals or produce any toxic by-products in the process. Ideally, the improved secondary explosive should be able to be produced in a procedure which is resource economical and doesn't "waste" chemicals. RDX (Hexogen) is one of the most commonly used military explosives, and has been used for decades for military applications. RDX is cheap to synthesize and shows very good energetic performance (pure RDX: VoD = 8833 ms^{-1}, p_{C-J} = 33.6 GPa, Q_{ex} = –5740 $kJ\ kg^{-1}$). However, RDX is relatively impact sensitive (7.5 J) and friction sensitive (120 N), which means that it doesn't show ideal values for safe handling. A further long-term issue with RDX is that it is toxic to both humans and the environment (the recommended limit in groundwater is a maximum of 2 $\mu g\ L^{-1}$) [11], which is a significant problem especially when considering the large scale on which it is produced. There are in addition, many more complex issues with current secondary explosives with respect to their application in specific situations. The problems outlined above for secondary explosives have acted as the motivation for the energetic materials research group at LMU Munich to strive towards the goal of developing new, even more powerful, less sensitive, and more ecologically and toxicologically compatible secondary explosives.

2. Design of new explosives

An ideal explosive must be designed in which many factors have been incorporated into the molecule. One of the most important of these is that the oxidizer (e.g. nitro groups, $-NO_2$ present) and the fuel (e.g. the carbon framework) are combined within the same molecule. This is the case, for example, in TNT, where the three nitro groups act as the oxidizer and the carbon-hydrogen framework provides the oxidizable component, i.e. the fuel. It is important for such molecules to be as endothermic as possible, since more

energy will then be released on detonation. Molecules such as TNT in which nitro groups are attached to a carbon framework can be made even more endothermic by altering the valence angles of the carbon atoms. Usually, tetrahedral carbon atoms have angles of ca. 109.5°. However, by forming rings or cages, the arrangement of atoms/groups around carbon atoms can be engineered to deviate significantly from this value, resulting in strain which contributes to increasing the endothermicity of the molecule. This is the case for two prominent secondary explosives. For example, octanitrocubane is a compound in which eight nitro groups are attached in total to the corners of cubane, meaning that each carbon atom in ONC has three 90° bond angles and is attached to three C atoms and one -NO_2 group. A consequence of the difficult synthesis of ONC - which has only produced ONC in very small quantities so far - is that it has not been investigated for use and remains currently of academic interest. Perhaps the best-known example of a secondary explosive which has a cage structure is CL-20 (Figure 1). Despite being one of the best-known non-nuclear explosives and having been developed around 30 years ago at the Naval Air Warfare Center China Lake, CL-20 has not yet found widespread use. This is due to both the high cost of the compound and its relatively high sensitivity towards external stimuli. A further issue that plagues CL-20 is polymorphism – unfortunately CL-20 exists in different polymorphs in temperature regions relevant to its use in the field. Phase changes are undesirable, since different phases can show different densities and specific volumes [11].

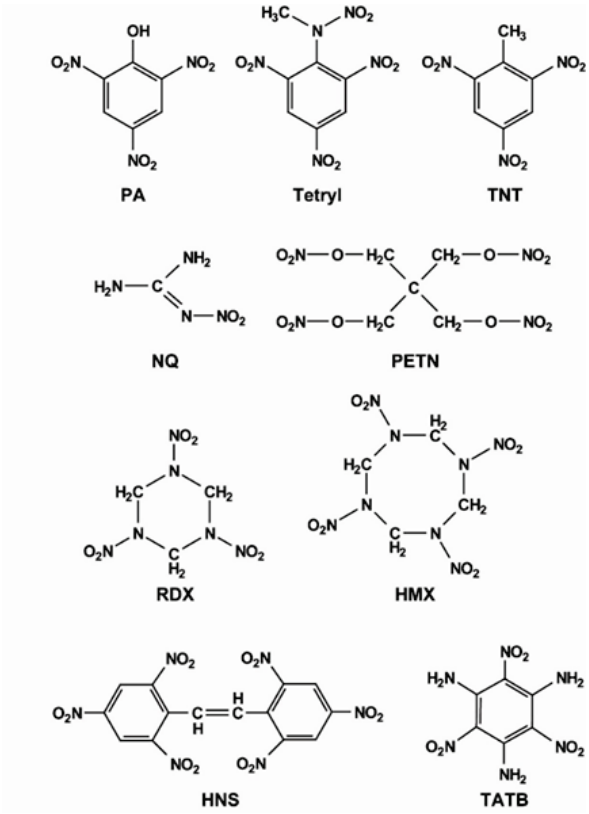


Fig. 1. Molecular structures of some secondary explosives

The synthesis of nitrogen-rich molecules follows a completely different concept ([16], [17], [17], [18], [19], [20], [21]). Nitrogen is unique in the periodic table in that the average bond energy per 2-electron bond increases from single to double to triple bonds (Figure 2), while the opposite is true for its neighboring element, carbon. Thermodynamically, acetylene (C_2H_2) would be expected to trimerize into benzene (C_6H_6), however, N_2 (isolobal to acetylene) would never be expected to trimerize at room temperature to form hexaazabenzene (N_6) [11].

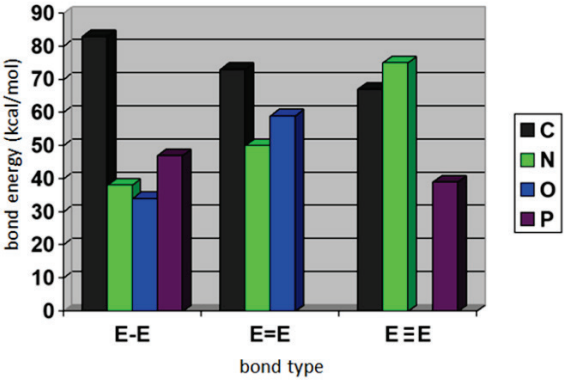


Fig. 2. Average element-element bond energies per 2-electron bond (in kcal mol-1).

Due to nitrogen showing the opposite trend in average bond energies per 2-electron bond (bond energies: C-C > C=C > C≡C but N-N < N=N < N≡N), any N-N bonds present in a molecule release a considerable amount of energy when they are converted into N≡N bonds in N_2. For this reason, nitrogen-rich molecules (N > 60%) with average N-N bond orders of < 2 are particularly of interest in the design and synthesis of new high-energy secondary explosives [11]. Even if a molecule has a high nitrogen content of 60% or 70%, and only few C-H units are present, these C-H units must be oxidized during the detonative process, and in order for this to occur, oxidizing groups, as are shown in Figure 3, must be present in the molecule. In order to oxidize one >CH_2 group, one -NO_2 group is required to convert the carbon into CO and the two hydrogen atoms into H_2O [11].

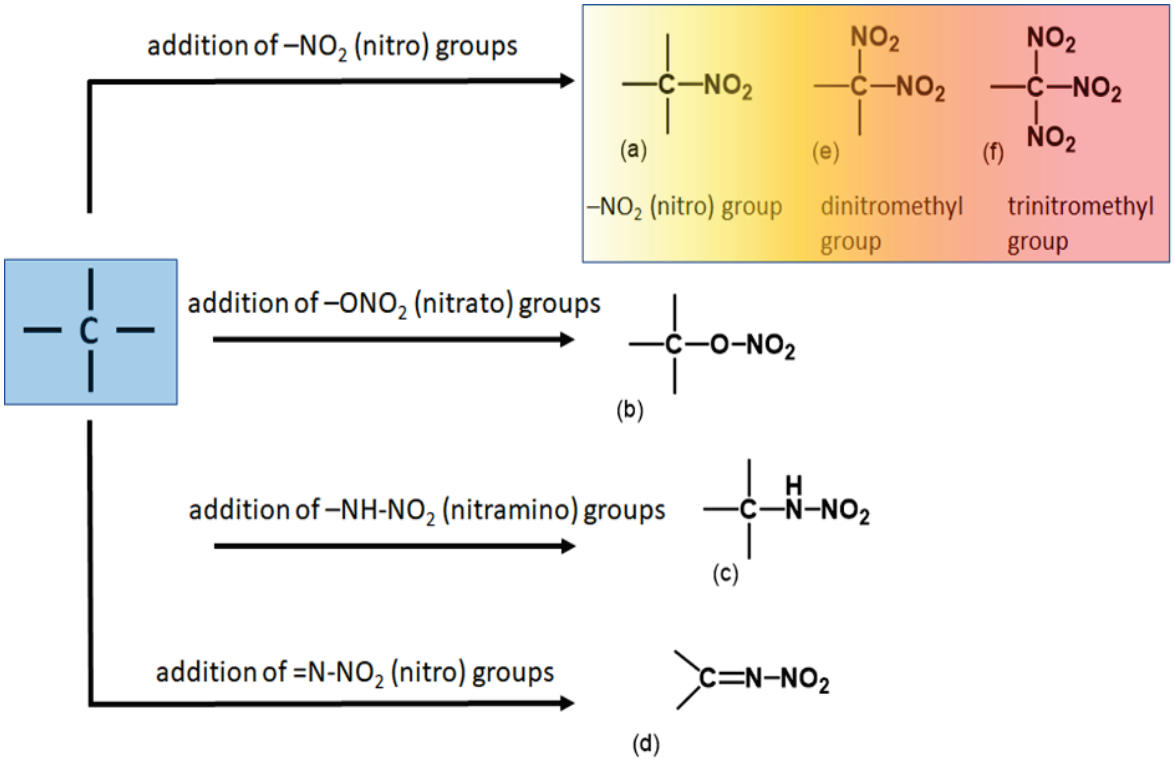
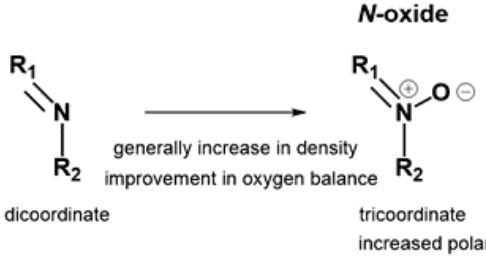


Fig.3. Possibilities for introducing oxidizing groups into an energetic material: a) nitro, b) nitrato, c) nitramino, d) nitrimino, e) dinitromethyl, f) trinitromethyl.

In addition to introducing oxidizing groups into a nitrogen-rich molecule, the oxygen balance of a molecule can be improved by incorporating the N-oxide or the N-O functionality. The oxygen balance describes the relative amount of oxygen excess or deficit (with negative sign "–"), to achieve a balanced ratio between the oxidizer and the combustible components (fuel). Therefore, the addition of oxygen to a trivalent nitrogen atom to convert it into an N-oxide functional group is an excellent possibility to increase the oxygen balance of the molecule, but without adding any other undesirable elements. Improving the oxygen balance is not the only reason that N-oxides have become popular target compounds. It has been observed that N-oxides generally show higher densities than the corresponding compound without the N-O group, which has been attributed to increased polarity of the N-oxides, due to the stronger intermolecular attraction associated with the >N+-O- group (Equation 1) [11]:



(1)

A high density is important for energetic materials, since the detonation velocity is proportional to the density, while the detonation pressure is even quadratically proportional to the density (Equations 2 and 3). This means that the incorporation of the N-oxide group which generally results in an increase in the density is also advantageous in this sense too.

$$P_{C-J} \propto \rho^2 \quad (2)$$

$$VoD \propto \rho \quad (3)$$

In terms of improving the stability of a secondary explosive, there are several approaches - and combinations thereof - which can be adopted, depending on whether the secondary explosive target compound is a neutral molecule or a salt. The three principal methods which are generally used are: (i) incorporation of a so-called push-pull mechanism, in which -NH_2 groups donate electrons into the system which are pulled by neighboring -NO_2 groups, (ii) stabilization through formation of π-delocalization or conjugation and (iii) formation of a salt instead of a neutral molecule, in order to increase stabilization due to the lattice energy. Examples of successful energetic push-pull system molecules are Fox-7 ($(H_2N)_2C{=}C(NO_2)_2$) or triaminotrinitrobenzene (TATB). A highly stable secondary explosive which is stabilized through π-delocalization is hexanitrostilbene (HNS). Fox-7, TATB and HNS are all used in military applications. One of the most exciting new secondary explosives to appear on the scene is dihydroxylammonium-5,5′-bistetrazolyl-1,1′-diolate (TKX-50) which is a salt, in contrast to the neutral molecules Fox-7, TATB and HNS. TKX-50 incorporates not only the nitrogen-rich and N-oxide formation strategies mentioned above, it also benefits in terms of stability from π-delocalization within the anion, and the lattice energy involved with being a salt.

3. Secondary explosives

Since TKX-50 is clearly one of the most promising new secondary explosives to have emerged in recent years, it is worth looking at why this is so in more detail. TKX-50, (Dihydroxylammonium-5,5′-bistetrazolyl-1,1′-diolate, Fig. 4, Tab. 1) was first synthesized in the energetic materials group at LMU Munich and published in 2012 ([22], [23], [24]). The potential of TKX-50 was immediately indicated by the energetic performance parameters which were predicted using the thermochemical computer code EXPLO5 [1], in combination with its sensitivity to external stimuli which were determined experimentally. Based on this initial selection criteria, TKX-50 immediately became of considerable interest for further examination and testing.

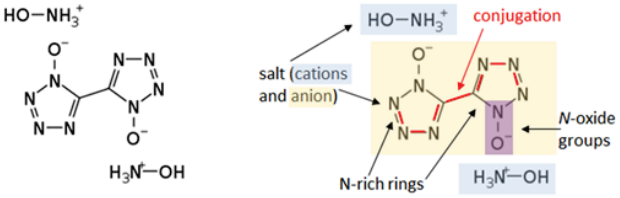


Fig. 4. Structure of dihydroxylammonium-5,5′-bistetrazolyl-1,1′-diolate, TKX-50

Table 1 shows that the density of TKX-50 at room temperature is high (1.877 gcm^{-3}) and the compound is endothermic with an enthalpy of formation of 197.4 kJ mol^{-1} [26]. The decomposition temperature is above 200°C which is good, and the sensitivity of TKX-50 to impact, friction and electrostatic stimuli all lie within accepted ranges for secondary explosives. The oxygen balance with respect to CO_2 (ΩCO_2) is only -27.1 % which is quite low, and is a consequence of the presence of two carbon atoms and 8 hydrogen atoms per salt equivalent and the absence of any oxidizing groups such as -NO_2, with only two N-oxide functional groups being present instead. Despite this, the energetic performance parameters of TKX-50 (VoD = 9649 ms^{-1}, p_{C-J} = 37.1 GPa, Qex = 4791 kJmol^{-1}) are excellent being superior or comparable than those of RDX (VoD = 8877 ms^{-1}, p_{C-J} = 34.5 GPa, Q_{ex} = 5745 kJmol^{-1}) and HMX (VoD = 9192 ms^{-1}, p_{C-J} = 37.8 GPa, Q_{ex} = 5699 kJmol^{-1}) (always at TMD).

Table 1. Structure of dihydroxylammonium-5,5′-bistetrazolyl-1,1′-diolate, TKX-50

Formula	$C_2H_8N_{10}O_4$
M/gmol^{-1}	236.2
IS/J	8 – 18
FS/N	120
ESD/J	0.1
$\Omega(CO_2)$/%	-27.1
T_{dec}/°C	crude: 221 recryst. from water: 237
ρ/gcm^{-3}	1.918 @ 100 K 1.877 @ room temperature
$\Delta H°_f$/kJmol^{-1}	197.4 mol^{-1}* (Paraskos, 2016, Schaller, 2020, Silva, 2023, Sinditskii, 2015,) 213 ± 20 kJ mol^{-1}(Klapötke, 2022) 175.3 ± 1.9 kJ mol^{-1} (Silva, 2023)

The original synthesis of TKX-50 was based on the N-oxidation of a C-C-linked bistetrazole, followed by the chromatographic separation of the formed isomers (Fig. 5). The N-oxide group was introduced using the oxidizer Oxone, which is the triple salt $2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$ which contains the active oxidizer potassium peroxymonosulfate, $KHSO_5$ [11].

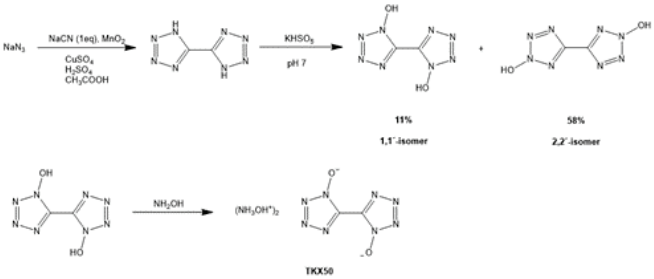


Fig. 5. Originally published synthesis of TKX-50 ([22], [25]).

Despite being a successful synthesis in the lab on very small scales, this method was not suitable for scale-up due to the separation of the isomers requiring column chromatography. Therefore, because of the promising properties that TKX-50 showed, considerable effort was invested into developing a new synthesis which was based on the chlorination and subsequent cyclization of glyoxime as shown in Fig. 6 and which would eliminate the problematic step.

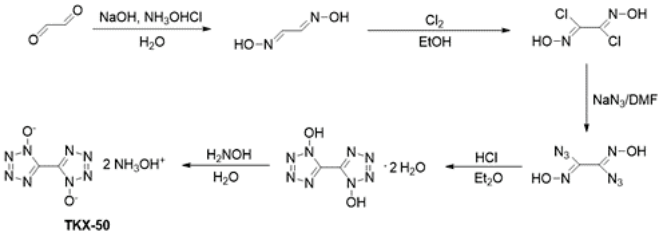


Fig. 6. Synthesis of TKX-50 starting from glyoxal ([23], [24]).

The second method shown in Fig. 6 avoids various isomers of the diole being obtained, which require separation. However, the synthesis in fig. 6 also has issues, since it requires isolation of diazidoglyoxime as an intermediate, and this compound, has the sensitivity of a primary explosive (IS = 1.5 J, FS <5 N, ESD = 76 mJ) and was therefore also not suitable for scale-up. The formation of

intermediates or by-products which have the sensitivities of primary explosives makes a synthetic method unsuitable for safety reasons, since primary explosives are much more sensitive to impact, friction and electrostatic discharge than secondary explosives are (typical values for primary explosives: IS = <4 J, FS = <10 N, ESD = 0.002 – 0.02 J). A further drawback of this synthetic route is the requirement of the gases chlorine (Cl2) and HCl which would also have been an obstacle to industrial production.However, in order to a secondary explosive to have a future for industrial production, a suitable synthetic route must be found. For TKX-50, another synthetic route was again developed by the energetic material group at LMU, which produces TKX-50 starting from commercially available glyoxime in the one-pot, 4-step reaction shown in Fig. 7 in an overal yield of approximately 85%. This synthetic route achieves the synthesis of TKX-50 from cheap, commercially available starting materials, in high yields, without requiring any explosive intermediates or separation of isomers, and also avoids the use of any gaseous reactant or toxic solvents ([27]). The ability to produce TKX-50 through such a route was a further milestone in the journey of TKX-50 from laboratory compound to possible industrial production.

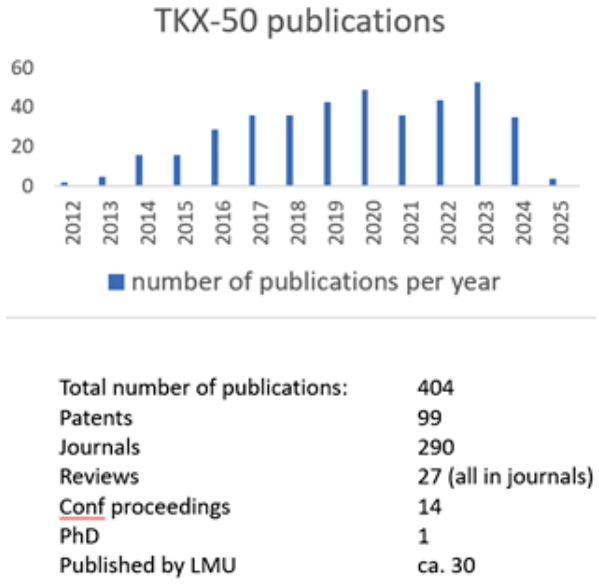


Fig. 8. Publications on TKX-50 up to January 2025.

The suitability of TKX-50 for application as a secondary explosive in warheads, shaped charges and similar applications has been a major focus of the published articles ([28], [29], [30], [31], [32], [33], [34], [35], [36], [37], [38], [39], [40]). A further aspect which has also received a lot of attention is the suitability of TKX-50 as an ingredient in solid rocket propellants has been studied extensively ([28], [41], [42], [43]). More recently, focus has been directed to the possibility of using TKX-50 in thermobaric compositions, and various theoretical and experimental investigations have been reported [44].

Recently, the behavior of TKX-50 in model thermobaric formulations was reported in which Aluminum was added to TKX-50 (Fig. 9). Experimental investigations were able to show that the addition of about 10% Al to TKX-50 resulted in a decrease in Qdet by about 90 Jg^{-1}. However, Al reacts with the detonation products of TKX-50 in an exothermic manner, and this energy contribution was calculated to be approximately 375 Jg^{-1}. A thermobaric mixture of TKX-50 charges containing 27% Al was shown to detonate, generating an overpressure in the argon-filled explosion chamber that was approximately 20% higher than that observed for only pure TKX-50 (Tab. 2). A 370 K higher maximum temperature of the TKX-50/Al explosion products in the argon-filled chamber was also observed for the thermobaric mixture than that measured after detonating only TKX-50. Aluminum oxynitride with a low nitrogen content has been found in the solid detonation products of aluminized TKX-50, but only when detonated in argon. When detonated in an air atmosphere, charges of the TKX-50/Al mixture generate significantly higher overpressure and radiant temperature values. Overall, burning aluminum in nitrogen provides little energy, and even if the concentration of nitrogen in the post-detonation products is much higher than that of oxygen, aluminum oxides are still preferentially formed (Fig. 9 and 10) [44].

Fig. 9. TKX-50 charge metallized with Al (left) and witness plate after detonation of the TKX-50/Al charge (right) (Klapötke, 2023).

The experimentally determined values for the maximum overpressure in the detonation chamber filled with air or with argon for pure TKX-50 and the thermobaric mixture of TKX-50/Al are summarized in table 2.

Table 2. Measured and calculated values for the maximum overpressure in the chamber [44].

	TKX-50		TKX-50/Al	
	Air	Ar	air	Ar
Δp_{max} [MPa]	0.63	0.48	0.81	0.58
Δp_{cal} [MPa]	0.97	0.70	1.14	0.92
$\Delta p_{max}/\Delta p_{cal}$ [%]	65	69	71	64

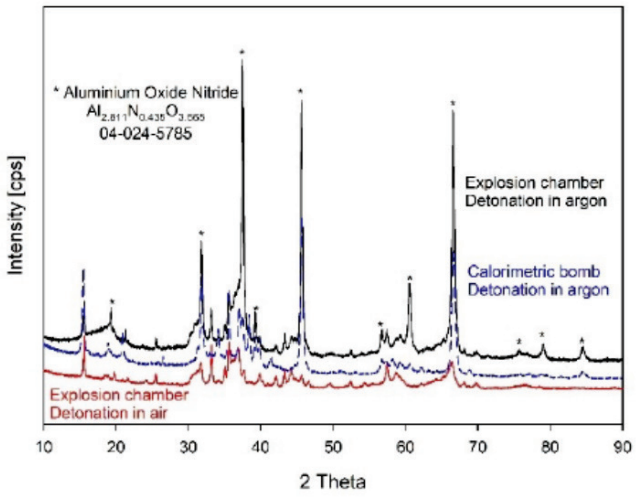


Fig. 10. XRD patterns of the solid detonation products of aluminized TKX-50 obtained in an Ar atmosphere (black and blue) and in an air atmosphere (red) [44].

Overall, it was found that a TKX-50 charge metallized with Al detonated in air shows a detonation pressure which is higher than if TKX-50 is detonated without Al. It is also the case, that a TKX-50 charge metallized with Al detonated in an argon atmosphere also shows a higher pressure than detonation of TKX-50 detonated in argon without Al [44].

Of the many challenges involved in investigating the properties of TKX-50, one challenge which posed many issues was determining the enthalpy of formation of TKX-50. The enthalpy of formation of TKX-50 was a source of debate in the literature until recently, when finally, a series of values indicated that the enthalpy of formation of TKX-50 is in the range of 175.3 kJ mol-1 (Silva, 2023) - 213 kJ mol^{-1} [45]. The average value for the enthalpy of formation of solid TKX-50 based on the combustion calorimetry measurements of several independent research groups is 197.4 kJ mol-1 ([26], [46], [47], [48]). Prior to the most recently measured enthalpy of formation value for TKX-50, the best experimentally determined value for the enthalpy of formation of solid TKX-50 using combustion calorimetry was $\Delta H°_f$(TKX-50, s) = 213 ± 20 $kJmol^{-1}$ [45] and was used for the following energetic performance data calculations. However, more recently, the value of 197.4 $kJmol^{-1}$ has been used instead and is currently the recommended value for the enthalpy of formation of solid TKX-50 [26].

As was stated previously, an accurate value for the enthalpy of formation is essential for predicting the energetic performance parameters of an energetic material. If a value for the enthalpy of formation is used which is too high, the VoD and pC-J will be predicted too high. Using the improved value for the enthalpy of formation of TKX-50 in the solid state [26] allowed the performance parameters of TKX-50 to be calculated, and be compared with the values which were recently determined experimentally. Not only is good agreement observed for the calculated and experimentally determined performance parameters, some of the values for TKX-50 exceed those of currently used secondary explosives (Tab. 3) [26]. Determination of the detonation velocity experimentally is not a trivial task, particularly for TKX-50, which has a large critical diameter. A consequence of this is that a large quantity of TKX-50 is required using a larger-scale experimental set-up [45] based on the short-circuit method (Figs. 11 and 12). The previously reported value for the detonation velocity of TKX-50 that had been determined experimentally was obtained using the LASEM method, which is a completely different approach requiring only a single crystal in contrast to the multigram quantities required for the more standard method that was more recently used ([49], [50], [51], [52], [53]).

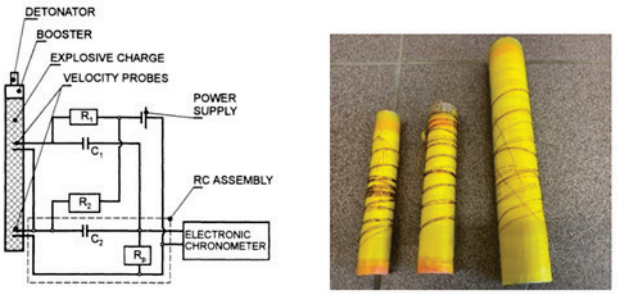


Fig. 11. A set of short-circuit items for measuring the detonation velocity of TKX-50 (left) and a schematic presentation of the short-circuit method which was used (right) [45].

Fig.12. Samples of TKX-50/Paraffin 97/3 granules before drying (left) and a set of pressed pellets of the same formulation (right) [45].

In the recent past, progress has also been made in obtaining more data regarding the sensitivity of TKX-50 to external stimuli. The most important physical data of TKX-50 are summarized in Tab. 3 for both the crude product, as well as for TKX-50 which was recrystallized from water. The basic sensitivity data which are generally presented for new secondary explosives are the impact and friction sensitivities as well as the sensitivity to electrostatic discharge. However, for compounds which show particular promise, there are many other sensitivity and stability data which must be determined, such as the long-term thermal stability, compatibility with relevant compounds and its performance in the slow cook-off as well as Koenen tests. All of these tests have been reported meanwhile for TKX-50. Furthermore, the performance of TKX-50 in model thermobaric formulations has also been very recently investigated in mixtures of TKX-50 with 10% micron-sized

aluminum powder (TKX-50/Al, 90/10) and 27% Al powder (TKX-50/paraffin/Al, 70/3/27) [44].

Table 3. Calculated performance parameters of TKX-50 compared to that of other secondary explosives ([45], [1]).

Explosive	ρ / gcm^{-3}	HE : wax	VoD / ms^{-1}	$p_{C\text{-}J}$ / GPa	Q_{det} / kJkg^{-1}
TKX-50	1.74	97 : 3	8919	30.0	4627
	1.877 (TMD)	100 : 0	9649	37.1	4791
RDX	1.74	97:3	8490	30.2	5561
	1.82 (TMD)	100	8877	34.5	5745
HMX	1.74	97:3	8472	29.9	5502
	1.905 (TMD)	100	9192	37.8	5699
CL-20	1.74	97:3	8506	31.4	5855
	2.038 (TMD)	100	9773	44.7	6231

The detonation characteristics of several explosive formulations based on TKX-50 have also been calculated, in which materials such as paraffin, HTPB, GAP, AMMO and BAMO were considered as fillers or binders ([35], [36], [37]). The influence of such fillers (with a volumetric content of up to 50%) on the detonation characteristics of the composite energetic materials was investigated (Fig. 13). In addition, the influence of porosity on the detonation characteristics of composite explosive formulations with a binder mass content of 5 and 10% has also been determined. The experimentally determined detonation velocities of three explosive formulations with inert and energetic binders showed good agreement could be observed between the calculated and experimental results for the detonation velocity (Fig. 14). A computational study of the explosion impact of charges of TKX-50 - as well as of explosive formulations based on TKX-50 containing the binders HTPB, GAP, AMMO and BAMO with 5% mass content of binder - on copper plates with a thickness of 1 mm and on layers with a thickness of 50 mm has also been reported. The charges (50 mm thick) and consisted of compact or porous materials with a porosity of 2% (Fig. 15). The EXPLO5 and Ansys Autodyn programs performed the thermochemical, thermodynamic and gas-dynamic calculations.

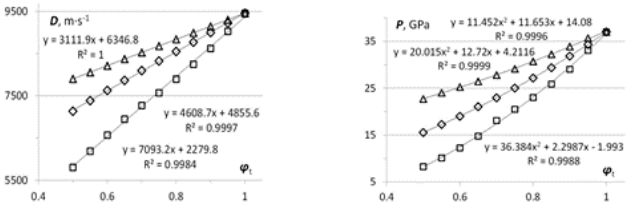


Fig. 13. Calculated values showing the influence of the volumetric content of TKX-50 on the detonation velocity (left) and detonation pressure ($p_{C\text{-}J}$) (right) of the energetic material TKX-50 (squares), as well as of the composite energetic materials with paraffin (rhombuses) and GAP (triangles) [37].

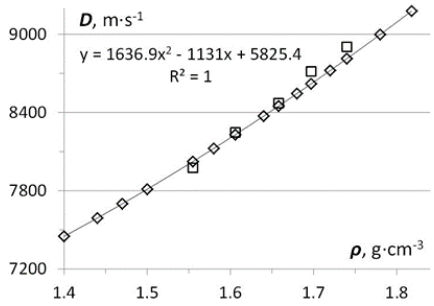


Fig. 14. Influence of the density of composition 1 (97% TKX-50 and 3% paraffin) on the detonation velocity: rhombuses - calculation, squares - experiment [37].

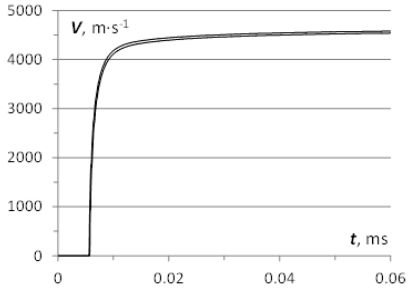


Fig. 15. Velocities of copper plates (1 mm thick) under explosive loading with charges with a paraffin binder (5%) 50 mm thick and a relative density of 100 and 98% ([18], [37]).

Moreover, a small-scale shock reactivity test (SSRT) was performed (Tab. 4), and the values of the relative dent size of TKX-50 were in good agreement with the calculated cylinder energies (Tab. 5) ([54], [55]).

The SSRT test procedure used is described in detail in the literature ([54], [55]) and is therefore only summarized here. An aluminium cylinder and steel cylinder (both 25.0 mm x 50.0 mm) are placed on top of each other (steel cylinder on top) and held together using crepe tape. The steel cylinder has a 7.5 mm hole from top to bottom in the center of the cylinder. A specific quantity of the explosive substance being tested is then filled into this hole and subsequently pressed by placing a steel pin (7.45 mm diameter) into this hole and pressing using a hydraulic press with 3 tons pressure. After repeating the pressing procedure twice, and removal of any explosive material residue in the hole after pressing and removal of the steel pin, the hole was cleaned

using a pipe-cleaner. The cylinder construction was then placed in a steel apparatus as is illustrated in reference [54], a Danadet-C2 detonator placed into the hole in the steel cylinder and initiated. The size of the dent resulting from the explosion was then measured using a profilometer. This procedure was performed twice per sample ([54], [55]).

Tab. 4. Results of a small-scale shock reactivity test (SSRT) showing the relative dent size of the tested compounds with respect to each other.

Explosive	mass [mg]	rel. dent size [volume in %]
RDX	504	69
CL-20	550	110
TKX-50	509	102

Tab. 5. Calculated cylinder energiesfor TKX-50 and RDX.

		% of standard			
compound	E_C / kJTATB cm^{-3}	PETN	HMX	Cl-20	
V/V_0					
TKX-50					
2.2	–8.16	168	128	109	90
RDX					
2.2	–6.94	143	109	93	77

Since the long-term stability is clearly an important factor when considering whether an energetic material is suitable for real-life applications, the stabilities of four commonly-known secondary explosives with real-life applications (RDX, HMX, CL-20 and PETN) were investigated and compared to that of TKX-50 [56]. Thermogravimetric analysis (TGA) measurements, using three different kinetic models (Ozawa-Flynn-Wall, ASTM E698 and Friedman) method were evaluated regarding their fit to the experimental data. To evaluate the samples with the NETZSCH Kinetics Neo software [57], thermal gravimetric analysis (TGA) measurements with a PerkinElmer TGA4000 were performed. In order to provide a consistent set of measurements, the samples were dried and sieved to keep them solvent free and within a uniform range of particle size. The measurements were performed at heating rates of 1 K min 1 (m = 2.071 mg), 2 K min 1 (m = 1.879 mg), 5 K min 1 (m = 2.285 mg) and 10 K min 1 (m = 2.105 mg) within a temperature range of 303 K to 673 K.

Using the Friedman method, the long-term stabilities for RDX, HMX, CL-20, PETN and TKX-50 could be predicted for each compound over 10 years (Fig. 16) [56]. In order to investigate the effect of different climate conditions on the stability of TKX-50 in storage scenarios, calculations were performed using climatic data for specific cities averaged over the past 30 years. In summary, the highest long-term stability can be predicted for CL-20 and the lowest for PETN (Fig 17). TKX-50 shows excellent longevity, with a slightly better behavior than RDX.

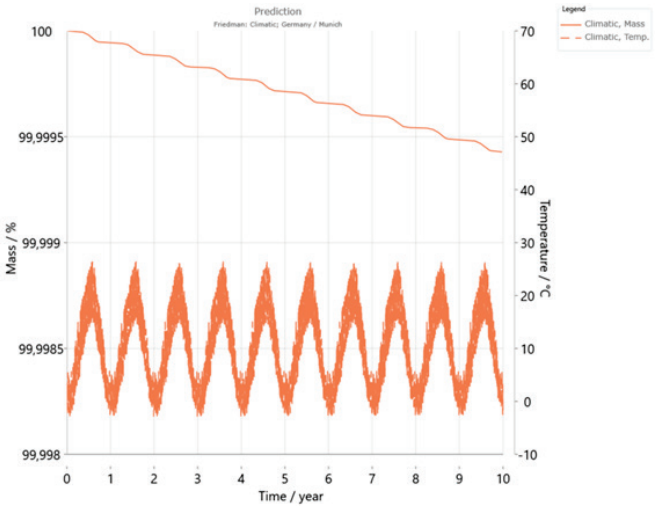


Fig. 16. Climatic prediction of TKX-50 for 10 years using the climate zone Munich [56].

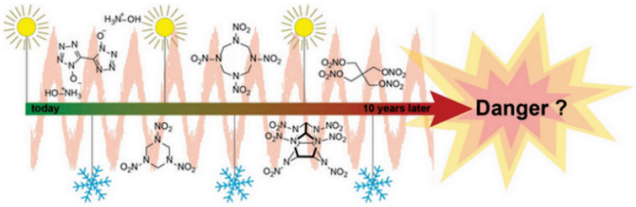


Fig. 17. Thermal aging behavior of different explosives [56].

In order to validate the calculated results, the five compounds were stored at 100°C for 4 weeks and their mass loss was investigated during this time. The obtained data was consistent to the kinetic predictions (Fig. 18).

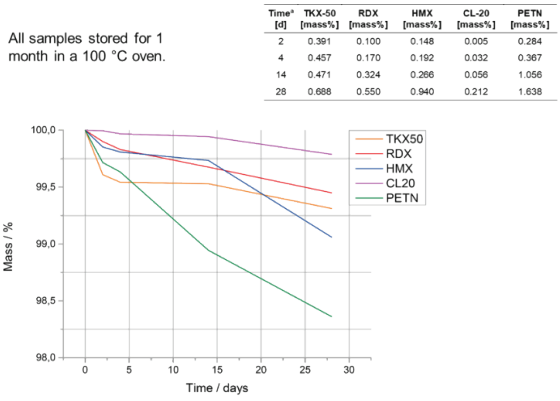


Fig. 18. Mass loss of common explosives at 100°C, over a four-week timespan [56].

In the introduction section it was stated that the environmental impact of energetic materials is one aspect which must be considered seriously for any new compound which aims to proceed to large-scale production. The REACH conform synthesis of TKX-50 shown in Fig. 7 is highly important in this context. Increasingly, the toxicity of the energetic material itself or the compounds used or produced in its synthesis, as well as its detonation products is a factor which is decisive in determining whether an

energetic compound has potential for real-life application. Tests performed on TKX-50 showed no signs of cytotoxicity for TKX-50. Furthermore, the results of mutagenic potential investigations also indicated that TKX-50 and its metabolites have no mutagenic effects on all tested strains of S. typhimurium and E. [58].

3. Oxidizers

In contrast to nitrogen-rich secondary explosives which have high percentage nitrogen contents, for oxidizers, a high percentage oxygen content is the goal. The synthesis of new oxidizers containing only the elements C, H, N, O is a challenging area, since the presence of each C atom and two H atoms requires two oxygen atoms in order to achieve an oxygen balance of zero with respect to CO. By far, the most widely used and standard oxidizer for all large-scale applications is ammonium perchlorate, NH_4+ClO_4- (AP). While AP has many properties that make it an excellent oxidizer, it unfortunately contains chlorine, which forms environmentally problematic HCl on combustion and in addition, perchlorate is of environmental concern. Therefore, there is considerable effort being made around the world to synthesize halogen-free oxidizers, with the goal of replacing the currently-used AP. Arguably, the synthesis and development of halogen-free green oxidizers is one of the areas of energetic materials which has made perhaps slower progress due to the challenges involved. Oxidizers which do not contain halogens, but which have properties equal to those of ammonium perchlorate have been a target for a long time. However, ammonium perchlorate (AP) has never been matched (Tab. 6). The values for AP are compared with those for the compound tris(2,2,2-trinitroethyl)orthoformate (which is commonly referred to in the energetic material literature as either 2,2,2-trinitroethyl formate or TNEF) in table 6.

Table 6. TNEF and AP main properties [28], [29], [30].

	TNEF	**AP**
Molecular formula	$C_7H_7N_9O_{21}$	NH_4ClO_4
Molecular mass [g mol^{-1}]	553.2	117.49
N [%]	22.8	11.92
$\Omega(CO_2)$ [%]	+10.1	+27.2
Heat of formation	−1,021 kJ kg^{-1}	−2,515kJ kg^{-1}

New oxidizers are a synthetic challenge, and the incorporation of larger quantities of oxygen into C,H,N,O generally requires the following aspects to be taken into account. First of all, it is difficult to synthesize C/H/N/O compounds with a positive oxygen balance since C and H require O atoms following the Springall-Roberts rules to form CO (or CO_2) and H_2O during combustion. This is especially true when considering the oxygen balance with respect to CO_2 (ΩCO_2), since in this case every C atom in the molecule requires 2 x O atoms (formation of CO_2) and every two H atoms require 1 x O atom (formation of H_2O) in order to reach ΩCO_2 = 0. Consequently, this means that every –CH_2 group present requires more than 3 x O atoms to have a positive ΩCO_2 value, meaning that, for example, pro -CH_2 group, 11/2 -NO_2 groups must be present. However, simply trying to overload a molecule with nitro groups is also problematic, since incorporating large numbers of nitro groups, especially –$C(NO_2)_3$ groups into a molecule risks lowering the thermal stability to a useless level ($T_{dec.}$ < 150°C). Secondly, although a highly positive oxygen balance is obviously on paper good for an oxidizer, it has been observed from testing oxidizers that higher oxygen balances generally result in higher impact sensitivities. An oxidizer which is highly impact sensitive would also not be useful for most large-scale applications.Despite these restrictive issues, progress has been made in halogen-free oxidizers, and out of all of the oxidizers which have been investigated by the energetic materials group at LMU, the best three examples are probably bis(2,2,2-trinitroethyl)oxalate [BTNEO] (1), 2,2,2-trinitroethyl-nitrocarbamate [TNENC] (2) and 2,2,2-trinitroethyl formate [TNEF] (3) (more correctly referred to as tris(2,2,2-trinitroethyl)orthoformate) (Fig. 19) ([59], [60], [61], [62], [63], [64]).

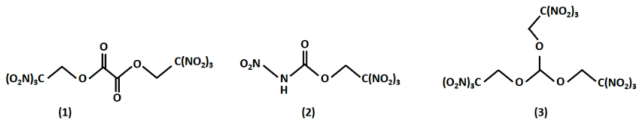


Fig. 19. New halogen-free CHNO oxidizers.

There are some aspects which are common to all three of these halogen-free oxidizers. In all three compounds no halogen is present, all are neutral molecules (AP is a salt), oxygen-rich -$C(NO_2)_3$ groups are present and O atoms have also been incorporated into the carbon skeleton to assist in achieving as positive an oxygen balance as possible. All three compounds possess a positive oxygen balance with respect to CO and CO_2 and have acceptable sensitivity parameters (Tab. 7). Unfortunately, the decomposition temperature of the nitrocarbamate (**2**) is only 153°C which is too low for application. This leaves the oxalate (**1**) and the formate (**3**) as the more promising candidates. The highly positive oxygen balance of 30.4% (with respect to CO), high density of 1.81 g cm^{-3} and a decomposition temperature of 192°C makes overall 2,2,2-trinitroethyl formate [TNEF] (**3**) the best candidate compound out of the three shown in Fig. 19. In addition, it should be mentioned that the sensitivity data of TNEF (IS = 5 J, FS = 9 N, ESD = 0.2 J) are within acceptable ranges. Therefore, TNEF was investigated further, and has already been scaled up in the lab to 100 g scale [65].

Tab. 7. Relevant data for the three oxidizers BTNEO (**1**), TNENC (**2**) and TNEF (**3**) ([28], [29], [30]

	BTNEO (1)	TNENC (2)	TNEF (3)
Formula	$C_6H_4N_6O_{16}$	$C_3H_3N_5O_{10}$	$C_7H_7N_9O_{21}$
M / g mol^{-1}	416	269	553
IS / J	10	10	5
FS / N	> 360	96	9
ESD / J	0.7	0.1	0.2
Ω(CO)/%	15.4	32.7	30.4
$\Omega(CO_2)$/%	7.7	14.9	10.1
m.p. / °C	115	109	128
T_{dec} / °C	186	153	192
ρ / g cm^{-3}	1.84	1.73	1.81
$\Delta H°_f$/kJmol^{-1}	-688	-366	-519

One aspect of oxidizers which is of particular interest currently is their use in thermobaric formulations. Recently, the suitability of TNEF (**3**) to replace ammonium perchlorate (AP) in thermobaric (TBX) formulations has been investigated computationally and experimentally. The thermobaric formulation which was chosen to be investigated consisted of the secondary explosive HMX, Al, binder and TNEF (*tris*(2,2,2-trinitroethyl) orthoformate) (TBX-2). In addition, the analogous formulation was made in which TNEF was replaced by the standard oxidizer AP (TBX-1), and the properties of the two formulations were compared. The formulations each consisted to 40% secondary explosive, 20% Al fuel, 20% binder and 20% of the oxidizer. The detonation velocity of the two thermobaric mixtures was both measured experimentally and calculated, and showed that the VoD of the mixture containing TNEF was essentially identical to that containing AP. Generally, both TBX-formulations showed similar energetic performance, with the formulation containing the halogen-free TNEF (TBX-2) having a slightly higher heat of detonation (Q_{ex}) and detonation temperature (T_{ex}), both of which are advantageous (Tab. 8, Fig. 20).

Table 8. Calculated energetic performance parameters (EXPLO5_V6.05.02) [1] of two TBX formulations (40% secondary explosive, 20% Al, 20% binder, 20% oxidizer) which vary only in the oxidizer used: oxidizer = AP (TBX-1), TNEF (TBX-2) [66].

	TBX-1	TBX-2
Oxidizer present	AP	TNEF
VoD / m s^{-1}	6699	6593
p_{C-J} / GPa	18.2	17.6
$-Q_{ex}$ / kJ kg	8202	8355
T_{ex} / K	4371	4451

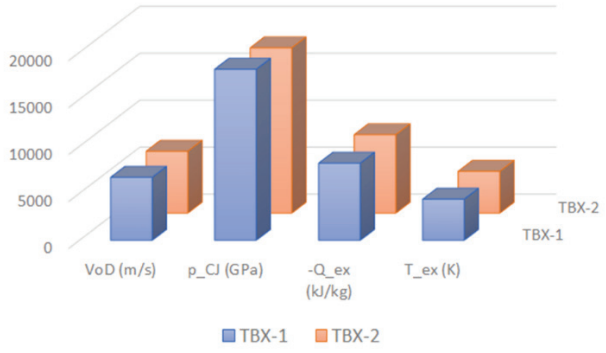


Fig. 20. Graphical representation of the performance parameters of formulation TBX-1 (containing the halogen-containing oxidizer AP) and TBX-2 (containing the halogen-free oxidizer TNEF).

Shock waves generated by the detonation of thermobaric weapons have a much longer duration than those which are generated by conventional high explosives. In addition, they also show a larger lethal radius. Under confinement, thermobaric detonations cause a series of reflected shock waves which maintain the fireball, and can extend its duration to between 10 and 50 ms, as exothermic recombination reactions occur. Due to its importance in the area of thermobaric formulations, the maximum overpressures generated from 600 g each of the formulations TBX-1 and TBX-2 were both calculated and experimentally measured as a function of the measuring spot distance from the center of the detonation (Fig. 21).

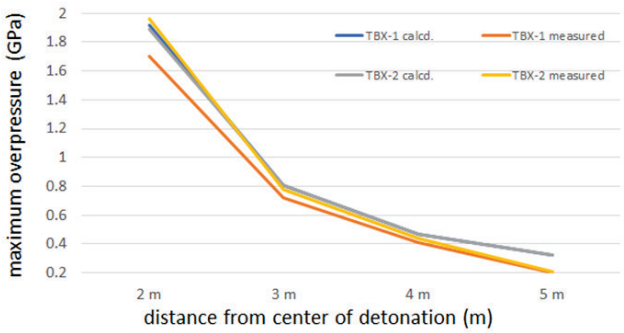


Fig. 21. The maximum overpressures generated from 600 g each of the formulations TBX-1 and TBX-2 as a function of the distance from the center of detonation.

Currently, the properties and performance of the TBX (TBX-2) containing the new, halogen-free oxidizer TNEF in the formulation are essentially as good as the same TBX formulation in which AP is present in the formulation (TBX-1) instead of TNEF. The advantage of using AP in the formulation is its cost, availability and the huge amount of information which is already known about many of the properties of AP. The disadvantage of using AP is that it contains chlorine, which forms HCl, which is problematic in terms of the environment, and contains the perchlorate ion which is problematic in terms of its effects on human health. Although in the early stages of development, using TNEF would eliminate both of these problems. However, much more work must be invested into TNEF before its potential for application can be reliably established.

4. Conclusion

An overview of the best secondary explosive (TKX-50) and oxidizer (TNEF) which have been developed in the energetic materials group at LMU shows has been given. The investigations and properties which have been discussed illustrate that extensive investigations must be performed before a compound can be truly classified as a candidate compound for potential future applications. While in the first instance several compounds may show good sensitivity to impact and friction and high calculated detonation velocities, this alone is not enough to categorize a compound as being a potential replacement for the currently-used HMX or RDX. TKX-50 act as an excellent illustrative example of the considerable factors which must be established for any energetic compound prior to its selection for up-scaling. In addition to considering the properties of pure TKX-50, extensive investigations have also been described into the suitability of TKX-50 for use as a secondary explosive in composite explosives and also in thermobaric formulations. The initial results from these investigations are highly promising. The difficulties in preparing new, halogen-free oxidizers with suitable properties are not identical with those

for developing new secondary explosives. The specific issues relevant to the development of new, environmentally more compatible oxidizers has been illustrated using the compounds BTNEO, TNENC and TNEF. Although TNENC has an excellent oxygen balance (which is essential for an oxidizer), unfortunately the decomposition temperature of TNENC is too low to make it of interest for further consideration. The safety, reliability and longevity of an oxidizer are essential properties. The oxidizer TNEF shows a particularly good combination of properties, and has therefore been increased to a 100 g scale for further investigation. The use of TNEF in a thermobaric formulation recently showed good performance and currently TNEF remains a promising candidate for use as an oxidizer in the future.

Acknowledgments
The author is indebted to and thanks the friends and colleagues listed below for their year-long, great and stimulating collaboration: Dr. Jasmin T. Lechner (LMU Munich & ICT Karlsruhe), Prof. Dr. Stanislaw Cudzilo (WAT Warsaw), Dr. Danica Bajic (Military Technical Institute, Belgrade), Prof. Dr. Muhamed Suceska (Zagreb University) and Dr. Vladimir Golubev (LMU Munich).

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