Pushing the limits of energetic materials – the synthesis and characterization of dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate†

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The safe preparation and characterization (XRD, NMR and vibrational spectroscopy, DSC, mass spectrometry, sensitivities) of a new explosive dihydroxylammonium 5,5′ bistetrazole 1,1′ diolate (TKX 50) that outperforms all other commonly used explosive materials is detailed. While much publicized high performing explosives, such as octanitrocubane and CL 20, have been at the forefront of public awareness, this compound differs in that it is simple and cheap to prepare from commonly available chemicals. TKX 50 expands upon the newly exploited field of tetryazine oxide chemistry to produce a material that not only is easily prepared and exceedingly powerful, but also possesses the required thermal insensitivity, low toxicity, and safety of handling to replace the most commonly used military explosive, RDX (1,3,5 trinitro 1,3,5 triazacyclohexane). In addition, the crystal structures of the intermediates 5,5′ bistetrazole 1,1′ diol dihydrate, 5,5′ bistetrazole 1,1′ diol dimethanolate and dimethylammonium 5,5′ bistetrazole 1,1′ diolate were determined and presented.

Introduction

The rational design of new energetic materials is a rapidly exploding field† with a long traditional rooting in the chemical sciences and a complexity that rivals that of the drug design. While the field has come a long way since the days of Liebig, Berzelius and Gay Lussac, and the concept of isomerism being determined from explosive silver fulminate and non explosive silver cyanate, current work in this field still follows the trend of its historic beginnings: that of simultaneous academic and practical interest and advances. In the quest for higher performing, safer, cheaper, greener, explosive materials, energetic materials chemistry must push the boundaries of the energy capacity of compounds, which requires new classes of compounds, new synthetic strategies, and advanced computational techniques. For example, the high nitrogen content of many advanced explosives has led to the preparation of new nitrogen nitrogen bond forming reactions and new heterocyclic systems in the quest for even higher performance.

In both civilian and military circles, the highest performing explosives make use of the same strategy: cyclic and caged nitramines. Belonging to the oldest class of explosives, those derive their energy from the oxidation of a carbon backbone by containing the oxidizer in the same molecule; RDX (1,3,5 trinitro 1,3,5 triazacyclohexane), HMX (1,3,5,7 tetranitro 1,3,5,7 tetraazacyclooctane) and CL 20 (2,4,6,8,10,12 hexanitro 2,4,6,8,10,12 hexaza isowurtzitane) all have fatal flaws that mandate replacement with modern explosives. Advanced energetic strategies allow for retention or improvement of the explosive performance, while avoiding the multitude of downsides present in these compounds: toxicity to living organisms (all), difficult and expensive synthesis (HMX, CL 20), high sensitivity to mechanical stimuli (all), and spontaneous changing of properties (CL 20). New strategies in the design of energetic materials include those with ring or cage strain, high heat of formation compounds, and compounds containing strong dipoles or zwitterionic structures. Unfortunately, the known materials with the highest detonation energy are often highly sensitive due to their unprecedented energy content, and are made via long and expensive pathways with a multitude of steps, making industrial scale up infeasible. For example, both DDF (dinitroazofuroxane) and ONC (octa nitrocubane) possess detonation velocities at the limit of known performances (around 10 000 m s⁻¹), however both are highly
sensitive and have more than 10 synthetic steps with exotic, expensive reagents used.15

A very promising explosphoric moiety in the design of new energetic materials is the tetrazole ring; the carbon on position 5 of the ring allows the facile attachment of various substituents for energetic tailorability, and the high nitrogen content and heat of formation of the heterocycle lead to high energetic performances. In order to improve the energetic properties of tetrazoles, several recently published studies showed that introduction of N oxides yields compounds with even higher densities and stabilities, lower sensitivities and better oxygen balances.5,7,11

Combining these principles with practical considerations in mind, a simple and secure synthetic pathway to the high per forming energetic material dihydroxylammonium 5,5’s biste trazole 1,1’ diolate (TKX 50) was devised.

Results and discussion

Synthesis (simple and scalable)

There are two major routes (A and B) to the 5,5’s bistetrazole 1,1’ diol (1,1 BTO) moiety (Scheme 1). The first (A) of which, the oxidation of the parent heterocycle with aqueous potassium peroxymonosulfate only leads to 1,1 BTO in poor yield (11%). The oxidation of the 5,5’s bistetrazolate anion with peroxo monosulfate was carried out in a manner similar to that we have previously reported for 5 nitro and 5 azidotetrazoles.5,10 Unfortunately, this reaction was found to produce the 2,2’ isomer as the major product, with only traces of the 1,1’ isomer which crystallized upon adding aqueous hydroxylamine.

After discovering the outstanding characteristics of TKX 50 as a high explosive, a different route to the precursor 5,5’s biste trazole 1,1’ diol was necessitated. Tselinskii et al.16 reported on the synthesis of the mentioned precursor 1,1 BTO from the cyclization of diazidoglyoxime under acidic conditions for the first time. Diazidoglyoxime is prepared from dichloroglyoxime in a chloro azido exchange reaction in DMF with more than 80 % yield, whereas dichloroglyoxime is prepared from glyoxime via chlorination in ethanol in high yield.

The problematic step here is the isolation of the highly friction and impact sensitive compound diazidoglyoxime, mandating a revised procedure before industrial scaled use. The problem was overcome by a procedure combining the formation and cycliza tion of diazidoglyoxime in one step in solution. Starting from commercially available glyoxal, the reaction process was trans formed into a five step, four pot synthesis to isolate TKX 50.

The prepared solution of diazidoglyoxime in DMF (impure with sodium chloride) is directly poured into diethylether and

Scheme 1 Synthesis of TKX 50 via oxidation of 5,5’s bistetrazole (A) and via cyclization of diazidoglyoxime (B).

HCl gas is bubbled through (Scheme 2). After cyclization of the azidooxime in the acidic medium the dimethylammonium salt of 5,5’s bistetrazole 1,1’ diol is formed by a reaction with dime thylene (formed by hydrolysis of DMF). After isolation and recrystallization of dimethylammonium 5,5’s bistetrazole 1,1’ diolate, it is dissolved in a sufficient amount of boiling water and combined with a solution of hydroxylammonium chloride, from which TKX 50 crystallizes first (Scheme 3).

An alternative procedure using NMP (N’ methyl 2 pyrrolidone) instead of DMF for the chloro azido exchange, followed by the same treatment, leads to the free acid 5,5’s bistetrazole 1,1’ diol which is then isolated as its sodium salt tetrahydrate upon the addition of aqueous sodium hydroxide and subseq uently treated with hydroxylammonium chloride in water. Starting from dichloroglyoxime, the overall yields of both procedures are very high with 72 % (DMF route) and 85 % (NMP route) for the synthesis of TKX 50. For a detailed description of all synthetic routes yielding TKX 50 and for all analytical data please refer to the ESI.†

X-ray diffraction

The crystal structure of TKX 50 was determined at three temperatures (100 K, 173 K, 298 K) in order to detect potential low temperature phase transitions and obtain precise densities (for explosive performance calculations). In addition the crystal structures of the intermediates 5,5’s bistetrazole 1,1’ diol dihy drate (recryst. from either water, MeCN, EtOH or glacial acetic acid), 5,5’s bistetrazole 1,1’ diol dimethanolate (recryst. from methanol) and dimethylammonium 5,5’s bistetrazole 1,1’ diolate (crystallized from H2O) were determined and are presented in the ESI.† Detailed crystallographic data and parameters of the measurements and solutions are given in Table S1.† The lack of observed phase transitions between 100 K and 298 K is advan tageous for energetic materials use as constant properties upon temperature changes result.

The density follows the expected trend of decreasing with increased temperature (100 K: 1.918 g cm⁻³ > 173 K: 1.915 g cm⁻³ > 298 K: 1.877 g cm⁻³). TKX 50 crystallizes in the monoclinic space group P21/c with two anion caton moieties in the unit cell. The molecular moiety of
It uses Becker Kistiakowsky Wilson’s equation of state (BKW EOS) for gaseous detonation products and Cowan Fickett’s equation of state for solid carbon (see ESI†). The input is based on the sum formula, calculated heats of formation (see ESI1) and the maximum densities according to their crystal structures (ESI, Table S1†).

With respect to the detonation velocity (Table 1), TKX 50 shows higher calculated values than all other mass produced and used explosives like 2,4,6 trinitrotoluene (TNT), RDX, HMX and CL 20. Looking at the detonation pressure, TKX 50 exceeds the values calculated for TNT and RDX and is comparable to HMX, but is slightly lower than for CL 20. Also in terms of potential use as a propellant mixture ingredient TKX 50 shows promising values due to its high nitrogen content. The calculated specific impulse using 60 bar isobaric rocket conditions is 261 seconds, which is slightly better than those of the other compounds in Table 1.

To assess the explosive performance of TKX 50 on a small laboratory scale, a small scale reactivity test (SSRT) was carried out (see ESI†) in comparison to CL 20 and RDX. Here, a defined volume of the explosive is pressed into a perforated steel block, which is topped with a commercially available detonator (Orica, DYNADET C2 0.5). Initiation of the tested explosive results in denting a separate aluminium block, which is placed right underneath the steel block (Fig. 2). From measuring the volumes of the dents (CL 20 $\cong$ TKX 50 $\Rightarrow$ RDX) (Table 2 in the ESI†), it can be concluded that the small scale explosive performance of TKX 50 exceeds the performance of commonly used RDX and is comparable to that of CL 20. The performance and safety characteristics for shipping of an explosive can be related to the data obtained from the Koenen test.¹⁸-¹⁹ The explosive is placed in an open ended, flanged steel tube, which is locked up with a closing plate with variable orifice (0–10 mm), through which gaseous decomposition products are vented (see ESI†).

Energetic performance

The performance data (Table 1) were calculated with the computer code EXPLO5.05 (latest version). EXPLO5.05 is based on the chemical equilibrium, a steady state model of detonation. The explosive performance data (Table 1) were calculated with the computer code EXPLO5.05 (latest version). EXPLO5.05 is based on the chemical equilibrium, a steady state model of detonation.

Table 1: Energetic properties and detonation parameters of prominent high explosives in comparison to TKX 50

<table>
<thead>
<tr>
<th>Formula</th>
<th>2,4,6 TNT</th>
<th>RDX</th>
<th>$\beta$ HMX</th>
<th>$\epsilon$ CL 20</th>
<th>TKX 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass [g mol⁻¹]</td>
<td>C₆H₈N₈O₈</td>
<td>C₆H₈N₈O₈</td>
<td>C₆H₈N₈O₈</td>
<td>C₆H₈N₈O₈</td>
<td>C₂H₈N₈O₄</td>
</tr>
<tr>
<td>IS [kJ</td>
<td>227.13</td>
<td>222.12</td>
<td>296.16</td>
<td>438.19</td>
<td>236.15</td>
</tr>
<tr>
<td>ESD test [kJ]</td>
<td>75 ²¹</td>
<td>75 ²¹</td>
<td>75 ²¹</td>
<td>75 ²¹</td>
<td>75 ²¹</td>
</tr>
<tr>
<td>FS [kJ]</td>
<td>535</td>
<td>120 ²¹</td>
<td>112 ²¹</td>
<td>48 ²¹</td>
<td>120</td>
</tr>
<tr>
<td>ESD test [kJ]</td>
<td>0.20</td>
<td>0.20</td>
<td>0.13</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td>$\Omega$ [%]</td>
<td>73.96</td>
<td>21.61</td>
<td>21.61</td>
<td>10.95</td>
<td>27.10</td>
</tr>
<tr>
<td>$T_{in}$ [°C]</td>
<td>81</td>
<td>205 ²²</td>
<td>275 ²⁴</td>
<td>279 ²⁴</td>
<td>215 ²³</td>
</tr>
<tr>
<td>$T_{in}$ [°C]</td>
<td>290</td>
<td>210 ²⁴</td>
<td>279 ²⁴</td>
<td>215 ²³</td>
<td>221</td>
</tr>
<tr>
<td>Density [g cm⁻³]</td>
<td>1.713 (100 K) ²⁴</td>
<td>1.858 (90 K) ²⁶</td>
<td>1.944 (100 K) ²⁸</td>
<td>2.083 (100 K) ²⁹</td>
<td>1.918 (100 K) ³⁰</td>
</tr>
<tr>
<td>Theor. $\Delta H^\circ$ [kJ mol⁻¹]</td>
<td>55.5</td>
<td>86.3</td>
<td>116.1</td>
<td>365.4</td>
<td>446.6</td>
</tr>
<tr>
<td>Theor. $\Delta U^\circ$ [kJ kg⁻¹]</td>
<td>168.0</td>
<td>489.0</td>
<td>492.5</td>
<td>918.7</td>
<td>2006.4</td>
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<tr>
<td>EXPLO5.05 values</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>$\Delta U^\circ$ [kJ kg⁻¹]</td>
<td>5258</td>
<td>6190</td>
<td>6185</td>
<td>6406</td>
<td>6025</td>
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<tr>
<td>$T_{K}$ [kK]</td>
<td>3663</td>
<td>4232</td>
<td>4185</td>
<td>4616</td>
<td>3954</td>
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<tr>
<td>$\rho_c$ [kbar]</td>
<td>235</td>
<td>380</td>
<td>415</td>
<td>467</td>
<td>424</td>
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<tr>
<td>$D$ [m s⁻¹]</td>
<td>7459</td>
<td>8983</td>
<td>9221</td>
<td>9455</td>
<td>9698</td>
</tr>
<tr>
<td>Gas vol. [L kg⁻¹]</td>
<td>569</td>
<td>734</td>
<td>729</td>
<td>666</td>
<td>846</td>
</tr>
<tr>
<td>$t_d$ [s]</td>
<td>205</td>
<td>258</td>
<td>258</td>
<td>251</td>
<td>261</td>
</tr>
</tbody>
</table>

* Impact sensitivity (BAM drophammer (1 of 6)). ² Friction sensitivity (BAM friction tester (1 of 6)). ³ Electrostatic discharge device (OZM research). ⁴ Nitrogen content. ⁵ Oxygen balance ($O = xO_2 + 2yC + 1/2zOH + (1600)$. ⁶ Decomposition temperature from DSC ($\beta = 5$ °C min⁻¹). ⁷ From X ray diffraction. ⁸ Calculated (CBS 4M method) enthalpy of formation. ⁹ Calculated energy of formation. ¹⁰ Energy of explosion. ¹¹ Explosion temperature. ¹² Detonation pressure. ¹³ Detonation velocity. ¹⁴ Volume of detonation gases (assuming only gaseous products). ¹⁵ Specific impulse using isobaric (60 bar) conditions.
vented. A defined volume of 25 mL of the compound is loaded into
the flanged steel tube and a threaded collar is slipped onto the tube
from below. The closing plate is fitted over the flanged tube and
secured with a nut. The decomposition is initiated
via thermal
ignition using four Bunsen burners, which are ignited simulta-
nously. The test is completed when either rupture of the tube or
no reaction is observed after heating the tube for a minimal time
period of at least 5 min. In the case of the tube’s rupture, the
fragments are collected and weighed. The reaction is evaluated as
an explosion if the tube is destroyed into three or more pieces. The
Koenen test was performed with 23.0 g of TKX 50 using a closing
plate with an orifice of 10 mm and caused the rupture of the steel
tube into approximately 100 pieces, the size of which reached
down to smaller than 1 mm from 40 mm (Fig. 3).

TNT destroys the steel tube up to an orifice width of 6 mm,
RDX even up to 8 mm.20 In order to get an “Interim Hazard
Classification” also a “Fast Cook Off test” (UN test 3d) was
performed in which TKX 50 underwent controlled deflagration
(no explosion occurred).

High safety  low sensitivity

Impact sensitivity is a high priority in explosive devices used in
the military due to the range of stresses devices may be exposed
to. The impact sensitivity of TKX 50 is 20 J which is much lower
than those for RDX, HMX and CL 20, which range from 4 to 7.5
J, and all three of which need desensitizing components added for
practical use. The low impact sensitivity of TKX 50 shows that it
can be used without desensitization.

Friction sensitivity is more important in the manufacturing
context, where TKX 50 with 120 N is of comparable or lower
sensitivity than any of RDX, HMX or CL 20, increasing the
margin of safety in the industrial context. Both the impact and
friction sensitivities of TKX 50 as compared to 2,4,6 trinitro
toluene (TNT), RDX, HMX and CL 20 are presented in Table 1.

The human body can generate up to 25 mJ of static electricity,
which can easily set off the most sensitive explosives such as lead
azide or silver fulminate. TKX 50 has an electrostatic sensitivity
of 0.100 J, which is far higher than the human body can generate,
allowing a comparable margin of safety when handling,
comparable to RDX or HMX.

Thermal stability is important for any explosive in practical use
as demanding military requirements need explosives that can
withstand high temperatures. For example, a munition sitting in
the desert can exceed 100 °C and for general use a component
explosive must be stable above 200 °C. TKX 50 with a decom
position onset of 222 °C easily surpasses this requirement (Fig. 4,
inset). This stability has been confirmed using a long term stability
test, where the sample is heated in an open glass vessel to a
temperature of 75 °C over 48 h to ensure safe handling of the
material even at elevated temperatures (Fig. 4, outer curve). The
lack of exothermic or endothermic events in the sample temper-
ature or heat flow curve implies that the compound is stable.

Toxicity environmentally friendly

One of the major aims in our search for new “green” energetic
materials is the low toxicity of the newly investigated compound

Fig. 2  Small scale reactivity test of TKX 50, RDX and CL 20. Above
pictures: test setup for the SSRT. Below: dented aluminium blocks after
initiation of the explosive with a commercial detonator.

Fig. 3  a) Koenen test experimental setup. (b) Parts of the Koenen steel
sleeve before and (d) after the test. (c) Moment of detonation.

Fig. 4  Outer curve: long term stability (TSC plot) of TKX 50 at a
temperature of 75 °C over a period of 48 h. Inner plot: thermal stability
of TKX 50 and RDX shown in the DSC plot (heating rate 5 °C min⁻¹).
is a representative species for other aquatic life and therefor a useful indicator when it comes to groundwater pollution. EC 50 is the effective concentration of the sample was determined. Vibrio fischeri luminescence of Vibrio fischeri to toxicitiy to RDX, as determined by the EC50 value for the decrease in toxicity to its contemporaries in currently used explosives such as RDX, TKX 50 is of lower sensitivity (mechanically and thermally) than and synthesized in an industrially viable process. Additionally, pushing the limits towards the most powerful explosives known, it itself, and of its degradation and decomposition products. In recent times the toxicity of energetic materials is a growing concern due to new understandings of the fate of explosives in the environment. The nitramine content of the ubiquitous RDX as well as less used HMX and CL 20 has been shown to be toxic to vital organisms at the base of the food chain, and in addition RDX is a probable human carcinogen. To assess the toxicity of TKX 50 to aquatic life, diluted aqueous solutions of the high explosive were subjected to the luminescent marine bacterium Vibrio fischeri using the commercially available bioassay system LUMIStox®. Vibrio fischeri is a representative species for other aquatic life and therefor a useful indicator when it comes to groundwater pollution. Being the most important toxicological parameter, the EC50 value of the sample was determined. EC50 is the effective concentration of the examined compound, at which the bioluminescence of the strain Vibrio fischeri is decreased by 50% after a defined period of exposure as compared to the original bioluminescence of the sample before being treated with the differently diluted solutions of the test compound. For RDX we observe an EC50 value of 91 ppm after an incubation time of 30 minutes. The herein determined EC50 value of TKX 50 of 130 ppm (Fig. 5 and ESI†) lies significantly above the EC50 value found for RDX indicating a lower toxicity to Vibrio fischeri, and as such, other aquatic life.

Conclusions

We have detailed the preparation of a new explosive, TKX 50 or dihydroxylammonium 5,5′ bistetrazole 1,1′ diolate. This material has exemplified the utility of the tetrazole N oxide chemistry by providing a new explosive material that is of very high performance (as calculated and demonstrated by SSRT testing), pushing the limits towards the most powerful explosives known, and synthesized in an industrially viable process. Additionally, TKX 50 is of lower sensitivity (mechanically and thermally) than its contemporaries in currently used explosives such as RDX, HMX and CL 20, making increased margins of safety when applied in practical use and devices. Finally, we have demonstrated the lower toxicity of TKX 50 compared to the nitramine RDX, as determined by the EC50 value for the decrease in luminescence of Vibrio fischeri. All of the characteristics of TKX 50 make it appropriate and exemplary to not just fulfill the long standing goal of a “green” RDX replacement, but also to replace it with a material of superior performance.

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Notes and references

30. X ray density (for details see CCDC 872231 and 872232).