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NEW SECONDARY EXPLOSIVES AND OXIDIZERS DEVELOPED AT LMU

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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 (TNEF) and bis(trinitroethyl) oxalate (BTNEO).*

1. INTRODUCTION

Many new secondary explosives are synthesized each year and reported in the scientific literature, however, very few of these compounds are of interest for actual real-life applications[1]. The steps necessary for investigating whether a new secondary explosive is suitable for translation from being a pure laboratory-scale compound to one which has potential for upscaling and being investigated as a serious potential candidate for use in real-life applications are rarely described in the literature. Since these post-initial considerations are rarely reported for new secondary explosives, the process from initial laboratory report to scale-up remains poorly described[2].

Initial reports on new explosive substances generally follow a relatively standard structure nowadays. Namely, the compound is synthesized on a less than 200 mg scale (for secondary explosives, considerably less for primary explosives), it is then characterized using standard characterization techniques used in the research laboratory for any class of compound, such as multinuclear NMR spectroscopy (typically 1H, 13C, 14N), IR spectroscopy and C/H/N analysis. Usually, but not always, the solid-state structure of the compound is determined using single crystal X-ray diffraction, which also provides a value for the density. For energetic compounds, additional factors are important and usually determined before the compound is reported in the scientific literature. These values are usually the decomposition temperature (T_{dec}.) using DSC or TGA, density from pycnometry, and in particular, the sensitivity of the energetic compound towards external stimuli such as impact, friction and electrostatics[3]. These values, combined with the calculated energetic performance parameters (VoD, PC-J, V0, Q_{ex}, T_{ex}) which are usually calculated using the program EXPLO5[4], provide a very good initial insight into an energetic compound. Inspection of the properties at this stage helps to drastically reduce the pool of reported compounds to a selected group of compounds which are still of interest as energetic compounds for possible applications. Most reported secondary explosive compounds don't make the cut for further consideration, either because the decomposition temperature is too low (it should be at least 200°C), or the sensitivity of the compound to external stimuli such as impact or friction is too high, or the calculated energetic performance parameters predicts a detonation velocity the same as or lower than HMX and RDX, which would therefore suggest that there would be no advantage to be gained in replacing HMX or RDX by the compound[2].

The very few compounds which meet these strict criteria require further, more specialized testing, in order to establish whether they are still of interest as an HMX/RDX replacement, or whether they too fail the cut at this second stage of testing. At this stage, there are a number of tests which can be performed. However, there are perhaps two main reasons why only very few compounds that pass the initial selection get investigated further. The first is that some testing equipment is very specialized and therefore not available to all synthetic energetic chemists[2]. A second aspect sounds trivial, but is a particularly tricky issue in synthetic energetic materials chemistry, and that is the necessity of handling only safe quantities, while at the same time, many of the more advanced, specialized tests require larger quantities than 200 mg of the compound, sometimes even several g[2]. Both of these issues strongly contribute to the trend of new energetic materials only being reported as far as the stage 1 characterization mentioned above, but then not further.

One result of this situation is that illustrative examples of energetic compounds being developed past the initial stages of characterization are relatively few and far between. Perhaps the most well-known examples of compounds which have in the recent past made the transition from initial testing to specialized testing and scale-up for applications are the secondary explosives Fox-7[5], LLM-105[6] and CL-

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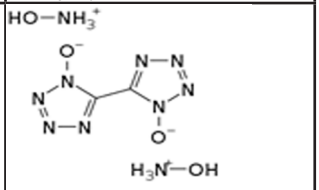
20[7]. Another secondary explosive which has undergone this transition is dihydroxylammonium-5,5′-bistetrazolyl-1,1′-diolate, TKX-50. Published for the first time in 2012[8], initial characterization immediately showed its potential for use[8]. The advances in research into TKX-50 have been rapid, and fueled by the large interest it has generated from groups around the world, such that in little over 10 years, TKX-50 is undergoing up-scaling by a company[9].

2. RESULTS AND DISCUSSION

TKX-50 is one of a large number of tetrazole compounds which have been synthesized with the aim of discovering a new secondary explosive[10]. The introduction of the N-oxide functional group to the tetrazole ring helps to improve the oxygen balance of the compound, while the resonance stabilization of the tetrazole rings increases the stability of the NN bonds with relatively low bond order[2]. The low sensitivity to impact, friction and electrostatics of TKX-50 combined with the high decomposition temperature and relatively high density at TMD (table 1) were initial positive indicators that TKX-50 was a particularly promising compound[8]. The enthalpy of formation of TKX-50 was initially overestimated[8], but the value of 194 kJ/mol corresponding to the average value from several independent measurements[11], combined with the high density, results in a calculated detonation velocity of 9649 ms-1, which is higher compared to that of HMX and RDX[12].

Table 1. Physical, sensitivity and energetic performance data for TKX-50[8], [11]

Formula	$C_2H_8N_{10}O_4$
Connectivity	
MWt. / g mol^{-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 / g cm^{-3}	1.918 @ 100 K 1.877 @ room temperature
$\Delta H°_f$ / kJ mol^{-1}	194 ± 20 kJ mol^{-1}

The original report on TKX-50 already contained data on many specialized energetic properties of TKX-50, such as the behavior of TKX-50 in the Trauzl test, ESD sensitivity, as well as toxicity data[8]. Possibly the most problematic initial aspect of TKX-50 was its synthesis, which required the synthesis and isolation of the explosive diazidoglyoxime, and which used chemicals which are not REACH conform. These two factors could have relegated TKX-50 to being an explosive compound which failed to pass stage 1 selection criteria[8]. However, an improved synthetic route was established which not only excluded the isolation of the explosive intermediate diazidoglyoxime, but also conformed to REACH guidelines and – equally important – was possible to scale-up safely[9].

Establishing the detonation velocity of TKX-50 was important to confirm the value predicted using EXPLO5. A value for the detonation velocity lower than that determined experimentally for RDX or HMX would also render TKX-50 to be of no significant improvement. As a consequence of the large critical diameter of TKX-50 (40 - 60 mm), determination of the detonation velocity requires a relatively large quantity of material, highlighting the importance of being able to prepare significant quantities of the compound. The VoD value of 8927 m s-1 determined experimentally for TKX-50 with a loading density of 1.73 g cm-3 agrees well with the calculated value and makes it higher in terms of detonation velocity than RDX or HMX and comparable with CL-20 (table 2)[12],[13],[14] .

Table 2. Calculated performance parameters of TKX-50 and other secondary explosives [4], [12]

Explosive	ρ / g cm^{-3}	HE : wax	VoD / m s^{-1}	pC-J / GPa	Q_{det} / kJ kg^{-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

A huge number of other investigations involving many aspects of TKX-50 by a large number of international research groups have been summarized recently in reviews[15].

One interesting recent aspect of TKX-50 is the possibility of using TKX-50 as the secondary explosive in thermobaric formulations[16]. Thermobaric explosives are a current important area of energetic materials, due to the improved incendiary and blast effects they produce in comparison to only the secondary explosive. Thermobaric explosives (TBXs) generally consist of a high explosive, polymeric binder, fuel (which is usually a metal powder such as Al or Mg or the Magnalium alloy) and an oxidizer (which is usually AP or AN)[17]. Recently, we have investigated the performance of TBXs in which two components of the thermobaric explosives were changed[16]. In one, the use of TKX-50 as the secondary explosive instead of the commonplace RDX or HMX was investigated both under a normal air atmosphere as well as under an inert atmosphere and in the second investigation, the performance of a TBX

in which the oxidizer AP was replaced by the chlorine-free C, H, N, O oxidizer TNEF was determined in an experimental study[18].

The performance of TKX-50 in the TBX formulations TKX-50/Al (90/10) and TKX-50/Al/Paraffin (70/27/3) was recently investigated[16]. The idea behind these TBXs was to investigate whether it would be possible to prepare TBXs free of additional oxidizer (i.e. AP or AN) in which a nitrogen-rich secondary explosive such as TKX-50 is used instead of the conventional choices of secondary explosive, HMX and RDX. By doing this, it was hoped that this would mean that the amount of additional oxidizer which is required for a traditional TBX could be reduced, meaning that the charge would be able to contain more secondary explosive by mass. It was hoped that the Al present would react with the nitrogen present in the nitrogen-rich TKX-50 to form aluminum nitrides, instead of the aluminum oxides formed when additional oxidizer is present in commonly used TBX formulations.

Experimental calorimetry measurements performed under an argon atmosphere found that the addition of 10% micron-sized Al powder to TKX-50 reduced the heat of detonation by around 90 J/g compared to pure TKX-50. However, the exothermic reaction of Al with the detonation products of TKX-50 is an exothermic process, contributing approximately 375 J/g[16]. The initial detonation products of TKX-50 mainly consists of N_2, CO_x, H_2O and smaller quantities of NO_2 and O_2. All of which can react with Al in the post-detonation stage in an exothermic reaction. Thermodynamically, the reactions between Al and O_2 or CO_x are preferred, however kinetically, reactions between Al and nitrogen are preferred due to the fact that the concentration of nitrogen is highest in the detonation products. Calculations predict that increasing the Al content of the TBX should result in an increase in the heat of detonation of the mixture, however it was found that initiation with a standard detonator was insufficient to cause detonation of TBX mixtures of TKX-50 with Al content of greater than 10%[16]. It was found for the TKX-50, 90/Al, 10 mixture that when the detonation was performed in an inert argon atmosphere (i.e. air is absent), the solid phase which was predominant was that corresponding to the formula $Al_{2.811}N_{0.435}O_{3.565}$, whereas this was not the case if the detonation was performed in an air atmosphere, whereby aluminum oxynitrides were essentially not observed[16]. For the detonations performed in an air atmosphere, it was found that the addition of Al to TKX-50 (TKX-50_{ph}/Paraffin/Al, 70/3/27) resulted in a 30% higher maximum overpressure value than for TKX-50_{ph} (TKX-50/Paraffin, 97/3) without aluminum metal, an increase in the maximum temperature of the explosion products in the chamber by 700 K, and the duration of time at which the temperature exceeds 1600 K was found to be three times longer (table 3)[16]. Therefore, it could be included that the addition of micron-sized aluminum powder to TKX-50 in a thermobaric mixture resulted in an improvement in the important performance values in comparison with the Al-free TKX-50 in an air atmosphere, and that due to the absence of aluminum oxynitrides in the solid phase detonation product for detonations performed in an air atmosphere, in the presence of oxygen (air), Al present reacts preferentially with oxygen present rather than nitrogen, even if the nitrogen content is high[16].

Table 3. Measured and calculated values for the maximum overpressure in the chamber for TKX-50 and TKX-50/Al mixture[16]

	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
Δp_{max} / Δp_{cal} [%]	65	69	71	64

As mentioned above, generally thermobaric mixtures contain an oxidizer which is usually AP and AN. AN and particularly AP are well-known and the most commonly used oxidizers. Not only does AP have an excellent oxygen balance (Ω_{CO} = 34%), it can be mass produced in an economically viable process, has a high density, high thermal stability good compatibility and can be stored for prolonged periods of time[2]. Furthermore, so much information has been accumulated over the years with respect to almost every aspect relevant to APs behavior as an oxidizer, it makes it a reliable and convenient oxidizer to use. However, it does have some drawbacks such as its more negative enthalpy of formation (-2536 kJ kg-1) than other oxidizers, as well as its heat of combustion (4587 kJ kg^{-1}) which is lower than that of, for example, its "greener" rival ammonium dinitramide, ADN (5145 kJ kg-1)[19]. ADN has one major advantage over AP, and that is the fact that it is an H, N, O oxidizer, whereas AP is a H, N, O, Cl oxidizer containing chlorine. Not only does AP contain chlorine, it is also water soluble, meaning that the perchlorate ion has been found in drinking water, and is suspected of interfering with thyroid gland function[2],[20]. Another health and environmental issue linked to AP is also due to the presence of chlorine, since on combustion, highly toxic and corrosive HCl is produced which forms acid rain. Despite these health and ecological concerns, AP is still the oxidizer of choice, but work is on-going to find halogen-free alternatives[2],[20].

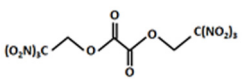
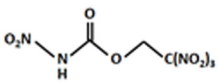
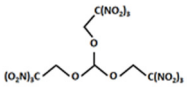
This is however, not an easy task, since the list of requirements for a compound to be considered a future, halogen-free, green oxidizer is long. A very high oxygen balance is obviously essential, good thermal stability, economical and easy synthesis on a large scale, low sensitivity to external stimuli, non-toxic, non-hygroscopic, halogen-free and ideally smokeless, as well as not showing phase changes in the solid state within the relevant temperature range. The latter issue along with the hygroscopic nature of AN are arguably its two major drawbacks for use – as well as the dangers in its storage[2].

Ammonium dinitramide is another compound under scrutiny for use as a green oxidizer, since in addition to

being halogen-free and possessing a high oxygen balance, it shows a high enthalpy of formation, burning rate and does not have the phase change issues in the solid-state which plague AN[20]. However, it is highly hygroscopic, has issues with thermal stability and also compatibility and cost of production. Hydrazinium nitroformate (HNF) has also been a forerunner in the race to replace AP, since it is non-hygroscopic, more endothermic enthalpy of formation than AP, high density and easy synthesis[20]. HNF has been known for over 70 years, however, issues still surround its thermal stability, as well as its sensitivity to external stimuli, as well as the health concerns surrounding compounds which could be release hydrazine which is carcinogenic[20].

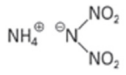
It is interesting to note that all of the above-mentioned compounds – AP, AN, ADN and HNF – are all salts. However, recently we have investigated three neutral compounds with high oxygen balances for their suitability for use as oxidizers. The three compounds which were found to be of most interest from this work are bis(2,2,2-trinitroethyl)oxalate [BTNEO] (1), 2,2,2-trinitroethyl-nitrocarbamate [TNENC] (2) and 2,2,2-trinitroethyl formate [TNEF] (3) (table 4)[21]. Each of these compounds contains at least one -$C(NO_2)_3$ group and are halogen-free, C, H, N, O oxidizers.

Table 4. Relevant data for the neutral C, H, N, O oxidizers bis(2,2,2-trinitroethyl)oxalate [BTNEO] (**1**), 2,2,2-trinitroethyl-nitrocarbamate [TNENC] (**2**) and 2,2,2-trinitroethyl formate [TNEF] (**3**)[21d]

	BTNEO (1)	**TNENC (2)**	**TNEF (3)**
Formula	$C_6H_4N_6O_{16}$	$C_3H_3N_5O_{10}$	$C_7H_7N_9O_{21}$
MWt. / g mol-1	416	269	553
Connectivity			
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
Ω(CO2) / %	+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
ΔH°f / kJ mol^{-1}	-688	-366	-519

An overview of the properties of these three compounds as well as those of HNF, ADN, AN and AP is given in tables 3 and 5. Common to BTNEO and TNEF are high densities and decomposition temperatures, whereas TNENC suffers from a relatively low decomposition temperature. Conversely, TNENC shows the highest oxygen balance followed closely by TNEF. TNEF has been scaled-up to produce 100 g, which was a necessary step in order to explore the possibility of TNEF being able to replace AP in a model thermobaric formulation[21d].

Table 5. Relevant data for the oxidizers HNF, AND, AN and AP[1],[20]

	HNF	**ADN**	**AN**	**AP**
Formula	CH_5N5O_6	$H_4N_4O_4$	$H_4N_2O_3$	H_4NO_4Cl
MWt. / g mol^{-1}	183.08	124.06	80.04	117.49
Connectivity	N_2H_5+C(NO_2)3-		NH_4+NO_3-	NH_4+ClO_4-
IS / J	4	4	40	15
FS / N	28	64	>360	>320

Ω / %	+13.11	+25.8	+19.99	+27.2
m.p. / °C	128	91.5	170	>220 (values vary)
Tdec / °C	131	135 (values vary)	210	389 (values vary)
ρ / g cm-3	1.88	1.812	1.722	1.95
ΔH°f / kJ mol-1	-71	-149	-367.5	-295.8

The thermobaric formulation investigated consisted of HMX as the high explosive, Al, binder and TNEF (40% HMX, 20% Al, 20% TNEF, 20% binder (TBX-2)) and was directly compared with the same mixture but in which the 20% TNEF oxidizer was replaced by 20% of the conventional oxidizer AP (TBX-1). Initial results show that TBX-1 and TBX-2 show very similar performance, even though AP in TBX-1 has been completely replaced by TNEF in TBX-2 (table 6)[18].

Table 6. Performance parameters of two TBX formulations (calculated with EXPLO5_V6.05.02) [4],[18].

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

Although there is much more work to be undertaken to assess whether TNEF has a future as an oxidizer in applications, initial investigations show that it has promising properties and is worth investigating further.

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