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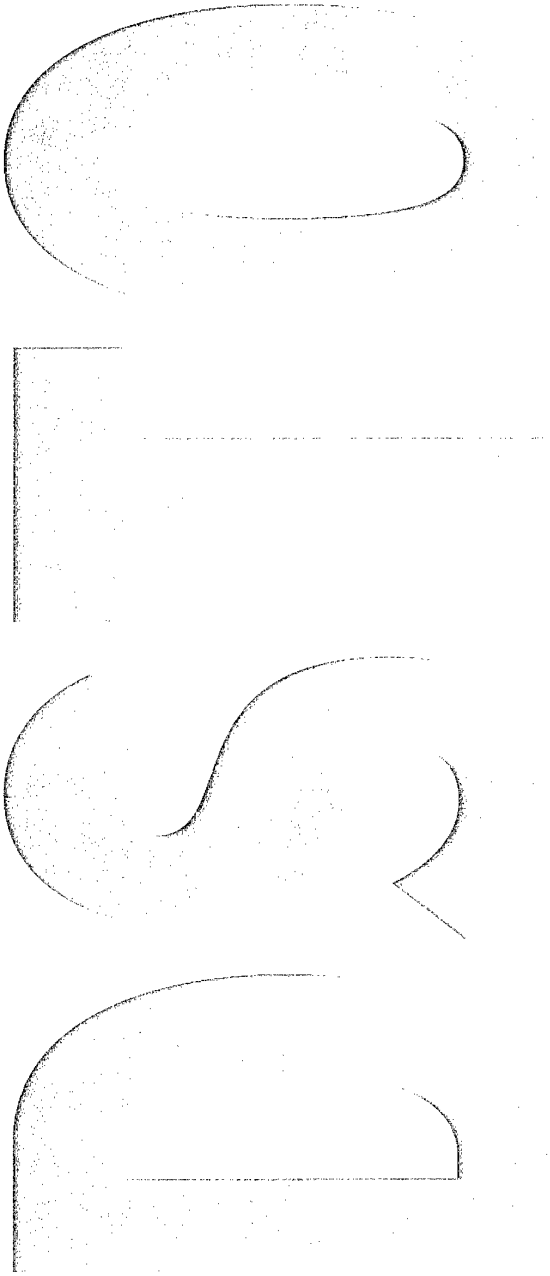

FOX-7 - A New Insensitive Explosive

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DSTO-TR-1238

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ABSTRACT

1,1-Diamino-2,2-dinitroethene (FOX-7) is an energetic material developed by FOI Sweden in the late 1990s. Theoretical studies have predicted that the performance of FOX-7 should exceed that of RDX. FOX-7 is also significantly less sensitive than RDX, particularly to impact and frictions stimuli. Consequently, FOX-7 is an attractive ingredient for application in high performance, IM-compliant explosive compositions. AMRL evaluation of FOX-7 has focused on the synthesis, hazards characterisation and performance studies. Aspects of these research areas, including preliminary experimental data that validates the theoretical performance values, are detailed.

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FOX-7 - A New Insensitive Explosive.

Executive Summary

1,1-Diamino-2,2-dinitroethene (FOX-7) is a new explosive ingredient with significant potential for application in high performance, insensitive munition (IM)-compliant explosive compositions.

The Swedish Defence Research Agency, FOI, developed FOX-7 in the late 1990s. The chemical synthesis of FOX-7 is relatively simple and has been investigated in the Aeronautical and Maritime Research Laboratory (AMRL). FOI have made improvements in the efficiency of the synthesis and transferred the technology to NEXPLO Bofors AB where a small pilot plant is operational. Chemical and physical characterisation of FOX-7 is underway with excellent preliminary results including good thermal and chemical stability. FOX-7 shows significant improvements in sensitiveness compared with RDX, particularly in its response to impact and friction stimuli. Theoretical studies, validated by recent experimental trials, predict that the performance of FOX-7 slightly exceeds that of the benchmark nitramine explosive RDX.

Future AMRL research directions are primarily focussed on the continued characterisation of FOX-7 including a more extensive study of the explosive properties. Examination of the relationship between particle properties (morphology, size and quality) and response to hazardous stimuli is also planned.

Authors

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After completing his PhD in synthetic and physical organic chemistry at Flinders University in 1996, Ian spent two years at The University of Melbourne as a post-doctoral fellow where he studied resin derived carbon composites. Since joining DSTO in 1998 he has been working in two main research areas: formulation, ageing and testing of polymer bonded explosives, and the synthesis, characterisation and testing of the insenstive explosive FOX-7.

Contents

Abbreviations

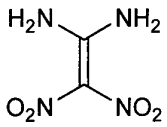
ARC	Accelerating rate calorimetry
Butyl-NENA	Butyl-2-nitratoethylnitramine
DMF	N,N-dimethyl formamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
EBW	Exploding bridge wire
ESD	Electrostatic spark discharge
EVA	*poly*(ethylene-*co*-vinyl acetate)
F of I	Figure of insensitiveness
FOI	Swedish Defence Research Agency
FOX-7	1,1-diamino-2,2-dinitroethene
GAP	Glycidyl azide polymer
HMDI	Dicyclohexylmethane-4,4'-diisocyanate
HMX	Cyclotetramethylenetetranitramine
HTPB	Hydroxyl terminated polybutadiene
IM	Insensitive munitions
K-10	2,4-dinitroethylbenzene (65%) and 2,4,6-trinitroethylbenzene (35%)
NMP	1-methyl-2-pyrrolidinone
NTO	3-nitro-1,2,4-triazol-5-one
RDX	Cyclotrimethylenetrinitramine
TATB	1,3,5-triamino-2,4,5-trinitrobenzene
TMD	Theoretical maximum density
TNT	2,4,6-trinitrotoluene
T of I	Temperature of ignition

1. Introduction

A major focus in research into energetic materials is the pursuit of improvements in insensitivity whilst maintaining or enhancing performance. This goal is consistent with the gradual adoption of Insensitive Munitions (IM) by defence forces around the world, including Australia [1]. Insensitive munitions are those which reliably fulfil their performance, readiness and operational requirements on demand, but in which the violence of response to unplanned hazardous stimuli is restricted to an acceptable level [1].

There are two general approaches to developing explosive formulations that satisfy IM criteria. One is to produce a polymer bonded explosive (PBX) in which the energetic component is incorporated within a flexible polymer matrix. The other is to use intrinsically less sensitive ingredients such as 1,3,5-triamino-2,4,5-trinitrobenzene (TATB) [2] or 3-nitro-1,2,4-triazol-5-one (NTO) [3, 4].

A recently developed explosive that falls into the later category is 1,1-diamino-2,2-dinitroethene (FOX-7 (**1**)).



(**1**)

Figure 1. FOX-7

The initial reports from the Swedish developers of FOX-7 [5-7] indicated that it is significantly less sensitive to hazard stimuli than cyclotrimethylene trinitramine (RDX) and slightly higher in performance.

The aim of this report is to review the synthesis and characterisation of FOX-7 as well as the early evaluation of FOX-7 as an energetic material. Work in progress within DSTO's Explosives Group is reported along with an outline of planned future investigations.

2. Production of FOX-7

2.1 Synthesis

The available literature describes only two general approaches to the synthesis of FOX-7, one of which was unsuccessful.

2.1.1 Amination of 1,1-diiodo-2,2-dinitroethene

In 1992, Baum and co-workers [8-10] reported the synthesis of 1,1-bisalkyl- and 1,1-bisaryl-amino-2,2-dinitroethenes by reacting 1,1-diiodo-2,2-dinitroethene (**2**) with primary amines (Fig. 2). The use of ammonia in this reaction scheme did not however lead to FOX-7.

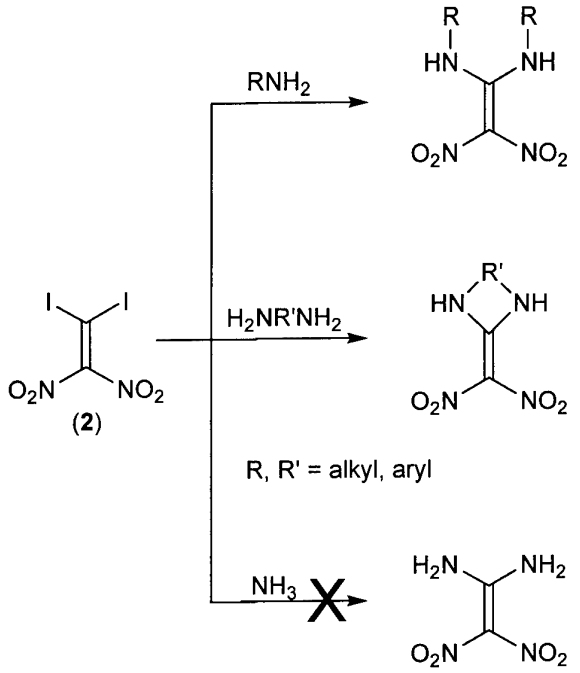


Figure 2. Synthesis of substituted dinitroethenes.

2.1.2 FOI Methods

In 1998 Swedish researchers from the National Defence Research Establishment, FOA (now the Swedish Defence Research Agency, FOI) published [5, 7] the synthesis of FOX-7. The general approach is outlined in Figure 3 and involves the nitration of a heterocyclic compound followed by hydrolysis to produce FOX-7. The nitration is carried out with mixed acid (sulphuric and nitric acids) at low temperature (< 30 °C) and the hydrolysis can be performed either by isolating the intermediate and

hydrolysing with aqueous ammonia or by adding the acidic mixture of the nitrated intermediate to water. At least three variations on the method have been trialled and are discussed below.

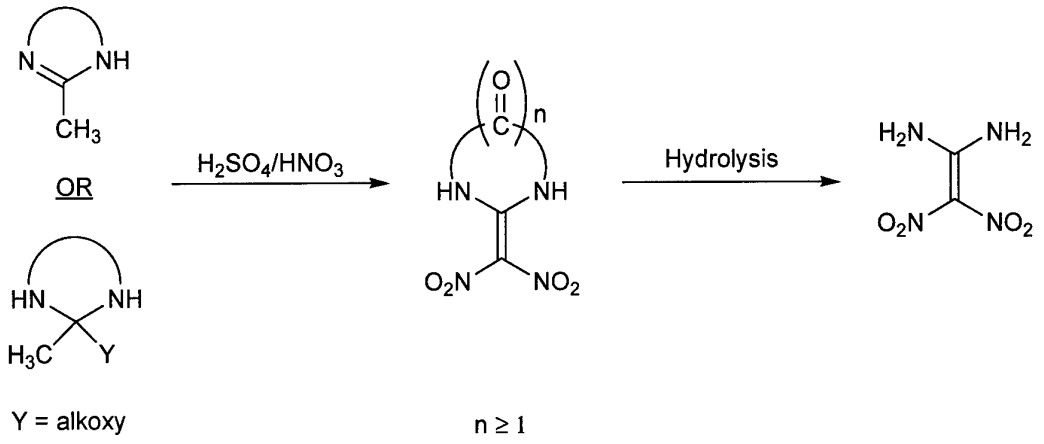


Figure 3. General method for the synthesis of FOX-7

2.1.2.1 *FOI Method 1*

Nitration of 2-methylimidazole (**3**) affords a thermally unstable intermediate with the proposed structure (**4**). Decomposition at ambient temperature or in solution results in the formation of the intermediate (**5**) in only about 15% yield. The hydrolysis with aqueous ammonia proceeds in excellent yield to produce FOX-7.

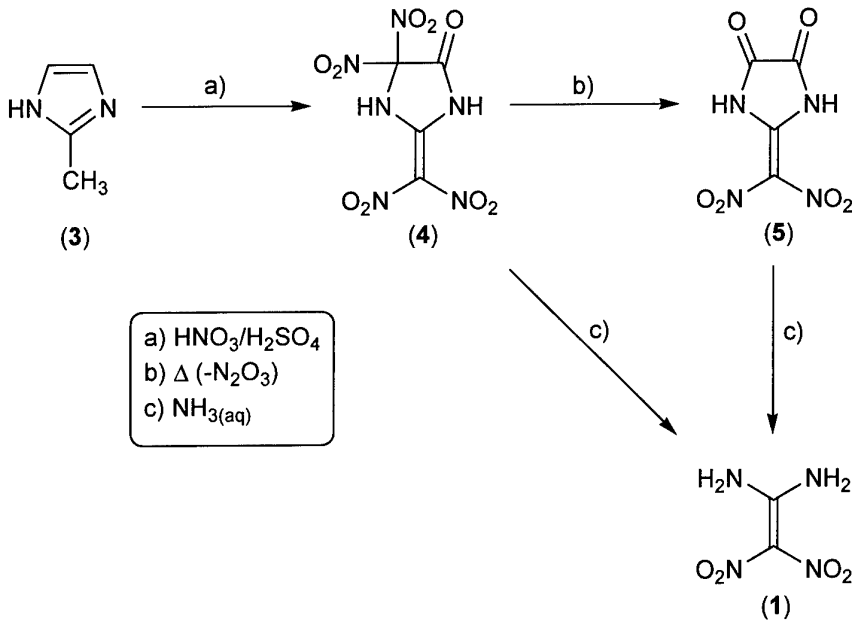


Figure 4. FOI Method 1

Two major factors disfavour this approach; 1) the intermediate (**4**) is a highly sensitive energetic material [5] and 2) the very inefficient nitration reaction results in an unacceptably low overall yield of ≤ 13%.

2.1.2.2 *FOI Method 2*

Condensation of diethyl oxalate with acetamidine hydrochloride at high dilution in methanolic sodium methoxide, followed by recrystallisation from methanol, produces the heterocyclic starting material 2-methoxy-2-methylimidazoledinedione (**6**). Nitration by conventional mixed acid methods produces the same intermediate (**5**) as in method 1 which is then hydrolysed to produce FOX-7.

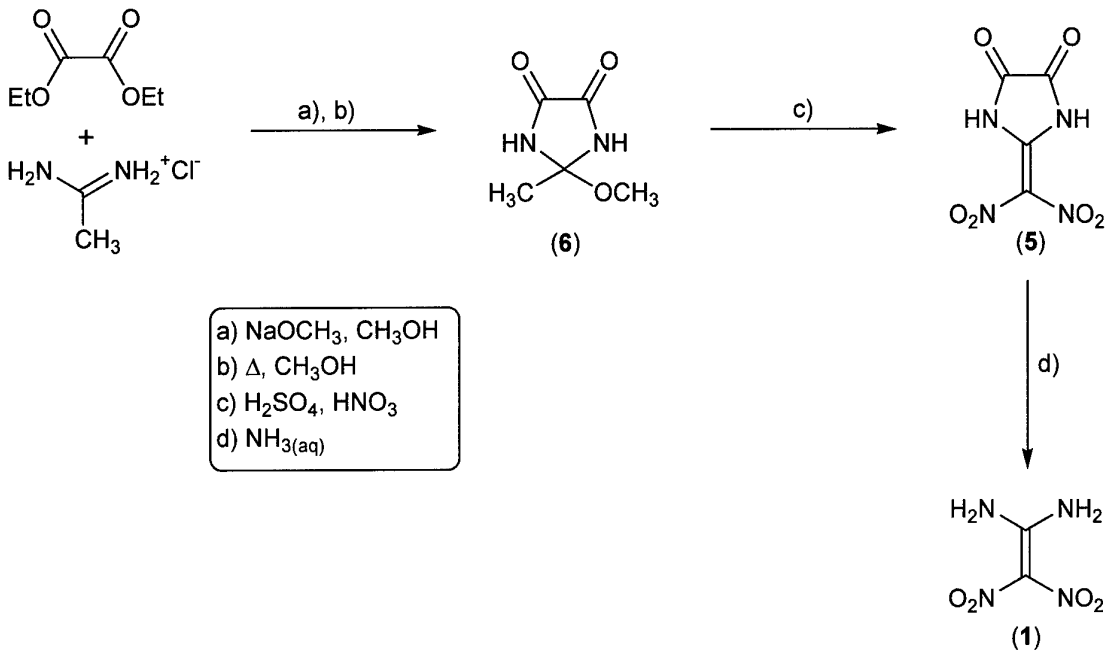


Figure 5. FOI Method 2

Whilst an overall yield of up to 38%† (58% from intermediate (6)) is a significant increase compared with the first approach, further improvement would still be required for it to be commercially viable. The high dilution required in the first step is also an inconvenience as large volume reaction vessels are required. Despite these two factors this is currently the preferred method for synthesis of FOX-7 and has been adopted at DSTO.

This process has been scaled up to produce approximately 50 g of FOX-7 in the DSTO laboratories (Appendix A); however at this larger laboratory scale an exotherm has been observed during the ammonolysis step, which can result in the product "frothing" out of the reaction vessel. No evidence of decomposition of the energetics has been observed and the yield is not reduced. This exotherm does not lead to a run-away reaction, but neither has its origin yet been identified, and it cannot yet be controlled. Currently the only effective way of handling this problem is to increase the size of reaction vessel to avoid overflow.

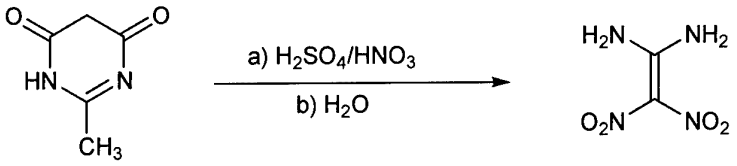
The purity of FOX-7 from either method 1 or 2 is typically excellent however on occasions contamination by oxamide ($H_2NC(O)C(O)NH_2$) was observed. Keeping the temperature of the ammonolysis reaction above about 20°C seems to eliminate the

† DSTO laboratories

formation of any oxamide. Recrystallisation from dilute hydrochloric acid removes the oxamide impurity if present.

2.1.2.3 *FOI Method 3*

The third method is understood to be the technique used in Sweden in the pilot-plant manufacture of FOX-7. Nitration of 2-methyl-4,6-pyrimidinedione (7) with mixed acid followed by aqueous hydrolysis affords FOX-7 [7, 11]. The yield in the pilot plant is around 80%. The precursor 2-methyl-4,6-pyrimidinedione is also produced in the same plant.



(7) (1)

Figure 6. Outline of FOI Method 3

2.2 Cost analysis

The estimated material cost for producing unpurified FOX-7 on a laboratory scale at DSTO via the preferred FOI Method 2 was calculated at ca. $300/100g (Table 1). This assumes the maximum overall yield of 38% and was based on current costs of materials in research quantities and does not consider plant, equipment or labour costs.

Table 1. Cost analysis to produce 100g of FOX-7 via FOI Method 2

Item	Amount Required	Cost (AU$)[a]
Methanol	7500 mL	25.00
Sodium Methoxide (30%)	1070 mL	35.00
Acetamidine Hydrochloride	168 g	89.00
Diethyl Oxalate	258 g	13.00
Hydrochloric acid	375 mL	7.50
Sulphuric Acid	940 mL	16.40
Nitric Acid	205 mL	3.20
Ammonia	190 mL	4.00
Ancillary Costs (estimated)		100
Total		293.10

[a] Cost based upon current prices from Crown Scientific and Sigma-Aldrich.

NEXPLO Bofors AB in Sweden are experimenting with the production of FOX-7 in batches of about 7 kg [11]. The product is granular in nature with an average particle size of about 25 microns. The procedure is based on FOI Method 3 and is carried out in a 600 litre reaction vessel. The reaction product is purified (> 99%) by recrystallisation from an organic solvent. This product is available for purchase at SEK32000 (ca. AU$5800) per kilogram [12].

3. Properties

3.1 General

FOX-7 has a molecular weight of 148.08 mass units and a formula of $C_2H_4N_4O_4$. It is stoichiometrically equivalent to RDX and HMX but structurally is not related. The density of FOX-7 has been determined by several means: 1.878 $g.cm^{-3}$ (crystal density [13]); 1.885 $g.cm^{-3}$ (powder diffraction [14]) and 1.86 - 1.87 $g.cm^{-3}$ (helium pycnometry, DSTO laboratories).

FOX-7 is poorly soluble in common organic solvents and water but readily dissolves in dipolar aprotic solvents such as dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF) [5] and 1-methyl-2-pyrrolidinone (NMP). Recrystallisation is possible from dilute hydrochloric acid, γ-butyrolactone or water with the acid being the most efficient of these media.

FOI have indicated [15] that FOX-7 may also be recrystallised from DMF or NMP (and presumably DMSO) by dissolving the FOX-7 in the solvent at 70 °C and then adding 4 - 5 equivalents of hot ethanol, methanol or water to precipitate FOX-7. The product from this recrystallisation is reported to have improved sensitiveness properties compared with unpurified FOX-7 (Section 3.3)

Microscopy (optical and SEM) and particle sizing has shown that FOX-7 particles produced directly from the reaction are typically around 30 micron with shapes from semi-amorphous tending to hexagonal crystals (Fig. 7 and 8). Recrystallisation from dilute hydrochloric acid typically affords hexagonal shaped crystals approximately 100 microns in diameter (Fig. 9 and 10).

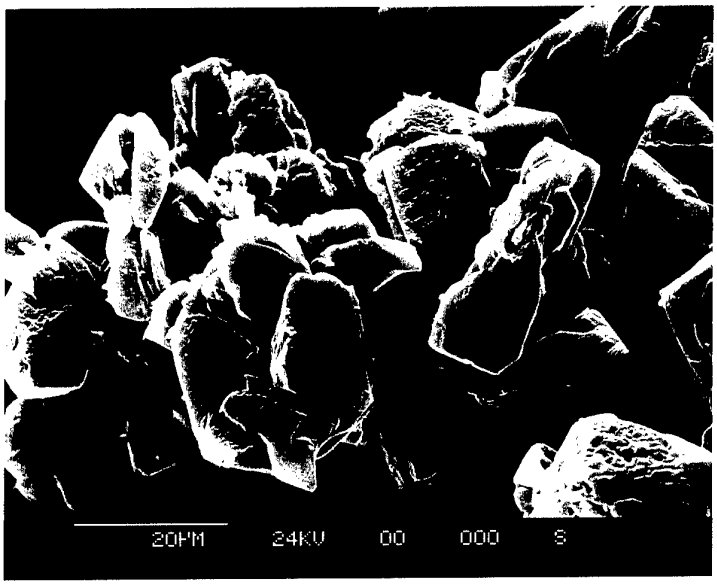


Figure 7. SEM image of FOX-7 isolated directly from reaction

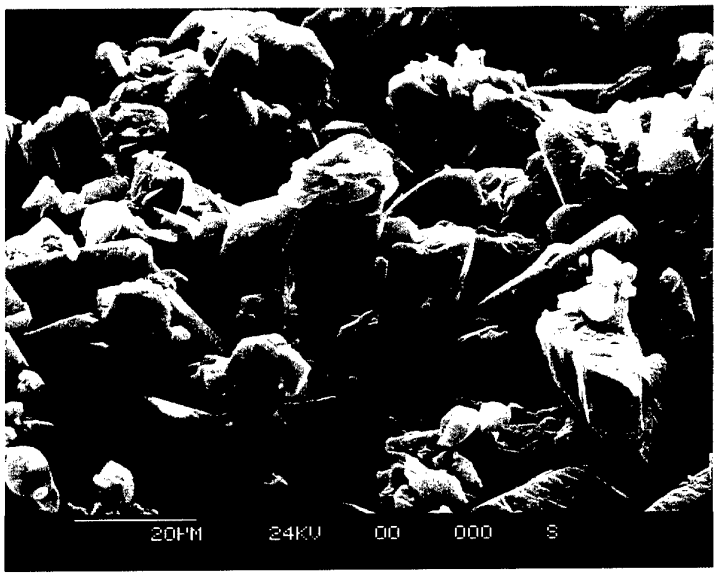


Figure 8. SEM image of FOX-7 isolated directly from reaction (different batch)

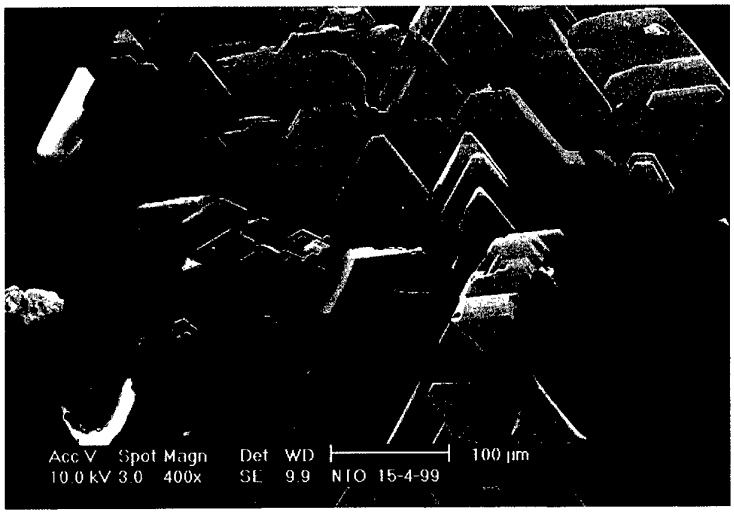


Figure 9. SEM image of FOX-7 recrystallised from 0.5M HCl

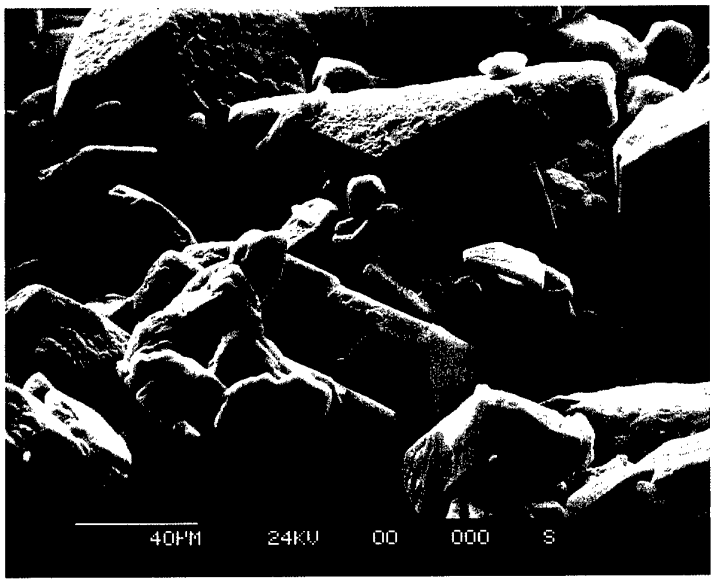


Figure 10. SEM image of FOX-7 recrystallised from 0.5M HCl (different batch)†

† Surface "bubbles" are from SEM coating process.

3.2 Instrumental analysis

3.2.1 Nuclear magnetic resonance spectroscopy

With only two carbon atoms and four identical protons the ^{1}H and ^{13}C NMR spectra of FOX-7 are extremely simple. In deuterated dimethyl sulfoxide, the single proton resonance for the amino protons occurs at approximately δ 8.8 ppm. The ^{13}C spectrum has two resonances, δ 128.3 and 158.3 ppm.

3.2.2 Infrared spectroscopy

The infrared spectrum of FOX-7 shows absorbances in the 3200 - 3400 and 1350-1650 wavenumber range characteristic of the amino and nitro functionalities as well as numerous peaks in the fingerprint region. Further details are reported in Appendix A.

3.2.3 Mass spectroscopy

Analysis of FOX-7 by electron impact mass spectroscopy at 70 ev showed two major peaks, the molecular ion at m/z 148 and the base peak at m/z 43. Numerous other minor fragmentations were also observed. Dorsett [16] discusses the relationship between the mass spectroscopy data and possible thermal fragmentation patterns. Bergman and co-workers have examined the mass spectra in greater detail [14] and interpret the strong molecular ion as being evidence that FOX-7 is more stable than RDX or HMX.

3.2.4 X-ray analysis

Bemm and Östmark from the Swedish Defence Research Agency, FOI, have carried out a detailed single-crystal x-ray diffraction study [6] of FOX-7. The major observations from the study were:

i) two intramolecular hydrogen bonds are present, each between an amine hydrogen and a nitro oxygen (Fig. 11).

ii) the nitrogen atoms in the nitro groups are out of plane (Fig. 11) with a twist of approximately 6°.

iii) the molecular packing is such that infinite two-dimensional layers are formed with extensive intermolecular hydrogen binding with the layers and weaker van der Waals interactions between the layers (Fig. 12).

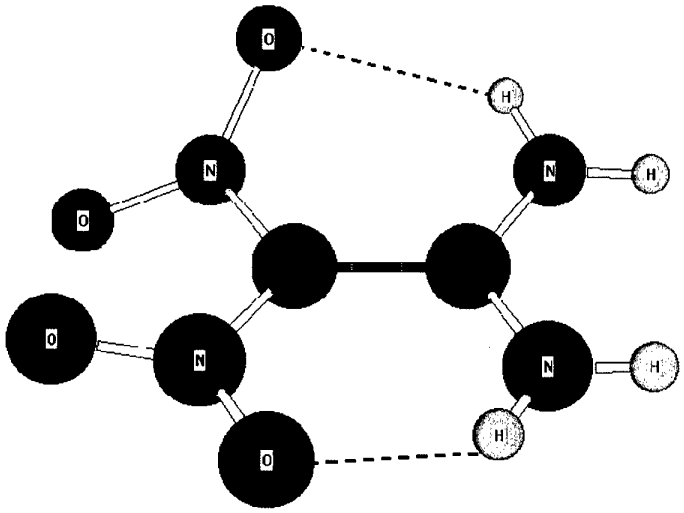


Figure 11. FOX-7 3D structure based on X-ray data

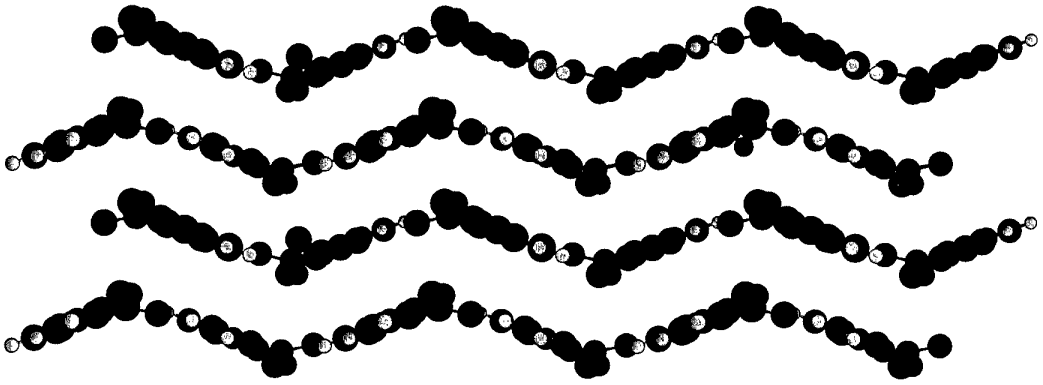


Figure 12. Representation of layered structure of FOX-7

The molecular packing structure with strong intra- and inter-molecular hydrogen bonding explains some of the physio-chemical properties of FOX-7, in particular low solubility, low sensitivity to impact and friction and the lack of melting point.

3.2.5 Calorimetry

The Differential Scanning Calorimetry (DSC) spectrum (Fig. 13) recorded at a heating rate of 5°C per minute showed two major exothermal peaks which occurred within the range of 214 - 238 °C and 250 - 276 °C (peak maximums), occasionally almost merging into a single peak. This is consistent with a two stage thermal decomposition. Additional minor endothermic peaks were observed at 112 - 115 °C and 165 - 172 °C, suggestive of thermally induced phase transitions. Thermogravimetric analysis [11] provides further evidence of a two-step process characterising the initial decomposition of FOX-7. No melting point is observed.

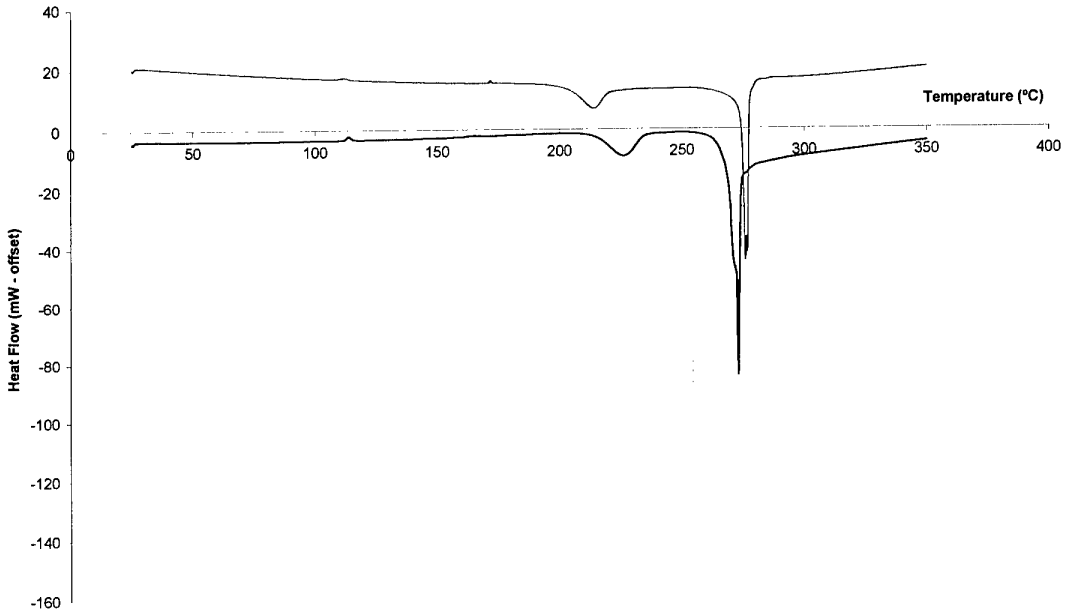


Figure 13. DSC traces for FOX-7 demonstrating variation between samples

The considerable variation in DSC spectrums of different batches of FOX-7 has recently been partially explained by Östmark *et al.* [11] by proposing a relationship between particle size and the decomposition temperature. The two major decomposition peaks were typically recorded at ~235 °C and ~280 °C however significant variations in the relative areas of these peaks, or complete disappearance of either peak was sometimes observed. Furthermore, the minor peaks were confirmed as phase transitions.

The heat of formation of FOX-7 was determined to be -32 kcal/mole by bomb calorimetry [13].

The activation energy of FOX-7 was calculated at 56 kcal/mole [11] following the relevant ASTM method [17]. Thermogravimetric analysis [11] provided further

evidence that a two-step process characterises the initial thermal decomposition of FOX-7.

Bergman and co-workers [14] undertook an Accelerating Rate Calorimetry (ARC) study to determine the onset and runaway temperatures for FOX-7 and RDX. Over the range of conditions trialled the reaction onset temperature for FOX-7 was 221 ± 2 °C and the runaway temperature was 230 ± 1 °C. For RDX the onset temperature was 197 ± 2 °C and the runaway reaction occurred at 201 - 202 °C. Significantly, the onset temperature for FOX-7 is higher than for RDX and RDX goes from onset to runaway faster than FOX-7.

3.3 Hazards Characterisation

The results of small-scale sensitiveness testing, in particular impact and friction testing, can be influenced by the purity, morphology and particle size of the sample being tested. The results of the tests are summarised in table 2.

3.3.1 Impact Sensitiveness

The figure of insensitiveness (F of I) by Rotter Impact analysis at DSTO was determined to be 110-140 for unrecrystallised FOX-7 and 80 for RDX with average gas evolution of 5.7 mL for FOX-7 and 11.9 mL for RDX. Swedish researchers have reported [5, 15] the impact sensitiveness of recrystallised FOX-7 to be 126 - 159 cm compared with 38 cm for RDX in the 2 kg BAM dropweight apparatus.

3.3.2 Friction Sensitiveness

The friction sensitiveness of unrecrystallised FOX-7 was determined on a Julius Peters BAM Friction apparatus at between 168 - 288 N. In comparison, the sensitiveness for a typical RDX sample is 120 N. The literature [5] value for purified FOX-7 is > 350 N (RDX=120 N) as recorded on a Julius-Petri apparatus.

3.3.3 Electrostatic Discharge Test

The electrostatic discharge (ESD) test is a safety test to screen the response of an energetic material to electrostatic discharges of 4.5 J, 0.45 J and 0.045 J. Ignition occurs at 4.5 J but not at 0.45 J for both FOX-7 and RDX.

3.3.4 Vacuum Stability Test

The gas evolution from a sample of FOX-7 held at 100 °C for 48 hours was determined to be ≤ 0.1 mL/g (RDX gave the same result). This result is a further indication of the excellent thermal stability of FOX-7.

3.3.5 Temperature of Ignition

The temperature of ignition of FOX-7 was determined (at a heating rate of 5 °C per minute) to be 226 °C, essentially identical to RDX at 223 °C. Literature values [13] for the temperatures of ignition of FOX-7 and RDX are 215 °C and 220 °C respectively, as determined by the Wood's metal bath technique.

3.3.6 Bickford Fuze and Train Tests

These tests provide an indication of the ease of ignition of an energetic material and the ability of the material to support a flame. Neither FOX-7 nor RDX ignited in the Bickford Fuze test. In the Train test FOX-7 ignited and supported the train steadily whilst RDX ignited but only supported the train for 110 mm.

3.3.7 Shock Sensitivity

Swedish researchers [13] used the NOL Small Scale Gap Test to determine the shock sensitivity of FOX-7 and other energetic materials. Without complete details of the charges it is difficult to accurately interpret the results however the implication is that FOX-7 has low sensitivity to shock stimuli.

3.3.8 Koenen Test

The Koenen test [18] is used to determine the sensitiveness of a substance to the effect of intense heat under high confinement. Swedish researchers reported [14] the results of the Koenen test for FOX-7 as being a type "F" reaction (explosion) at 6 mm nozzle diameter. RDX was more sensitive in this test, resulting in an explosion at 8 mm nozzle diameter.

Table 2. Summary of sensitiveness and hazard testing results

Test	FOX-7	FOX-7 (recryst.)	RDX
Rotter Impact (FofI)	110-140 [a]		80[a]
Dropweight Impact (cm)		126 - 159 [5, 15]	38
BAM Friction (N)	168-288 [a]		~120 [a]
Friction (N)		> 350 [5]	120
ESD - Ignition (J)	4.5 [a]		4.5 [a]
ESD - No Ignition (J)	0.45 [a]		0.45 [a]
Vacuum Stability (mL/g)	≤ 0.1 [a]		≤ 0.1 [a]
Temp. of Ignition (°C)	226 [a]		223 [a]
Bickford Fuse	Fails to ignite [a]		Fails to ignite [a]
Train Test	Ignition [a]		Ignition [a]
NOL SSGT (mm) [13]		6.22	9.33
Koenen Test [14]		6mm/"F"	8mm/"F"

[a] DSTO laboratories

3.4 Compatibility

Östmark *et al.* [13] determined the compatibility between FOX-7 and a number of other compounds by measuring the heat flows in a micro-calorimeter. Initially the thermal stability of FOX-7 was determined to be 0.37 J/g, which is considered very stable. FOX-7 was then tested with a range of binders (including HTPB and GAP), the isocyanate HMDI and the energetic plasticisers butyl-NENA and K-10. All materials showed excellent compatibility with FOX-7 with the exception of HTPB (R45-HT) for which the incompatibility was classified as very low[†]. The compatibility of FOX-7 with TNT (as a 1:1 mixture) was tested at DSTO by the vacuum thermal stability method (100 °C for 48 hours). The combined samples were as stable as the individual components under these conditions. These preliminary results indicate that the use of FOX-7 in polymer bonded explosives and in TNT melt-cast formulations should not present any compatibility problems.

3.5 Discussion

The results of the instrumental analysis and of the hazards characterisation show that FOX-7 is thermally quite stable and in almost all situations is significantly less sensitive than the benchmark RDX. The results for impact and friction sensitiveness clearly demonstrate the promise of FOX-7 as an insensitive ingredient with recrystallised FOX-7 being up to four times less sensitive than RDX. The comparison with RDX is

[†] It is believed that this minor incompatability may have been due to an impurity in the HTPB sample and does not reflect the true compatability between FOX-7 and HTPB.

particularly relevant as studies (Chpt. 4) predict that the performance of FOX-7 slightly exceeds that of RDX.

4. FOX-7 as an Energetic Material

4.1 Explosive Properties

4.1.1 DSTO evaluation of the performance of FOX-7

4.1.1.1 Theoretical

The software package CHEETAH (v2.0) uses traditional Chapman-Jouget thermodynamic detonation theory to predict velocity of detonation and detonation pressure values for ideal and mildly non-ideal explosives. Calculations were performed for FOX-7 and RDX (Table 3). The heat of formation used in the calculations for FOX-7 was -32 kcal/mole [5].

4.1.1.2 Experimental

FOX-7 was coated with 5% EVA (*poly*[ethylene-*co*-vinyl acetate], 40 wt% vinyl acetate, Aldrich) using a slurry process [19, 20]. Free flowing granules 100-500 microns in size were obtained. SEM analysis (Fig. 14 and 15) showed that the coating on the agglomerated particles was not homogeneous however it was deemed suitable for the application. Grade A RDX was coated by the same technique.

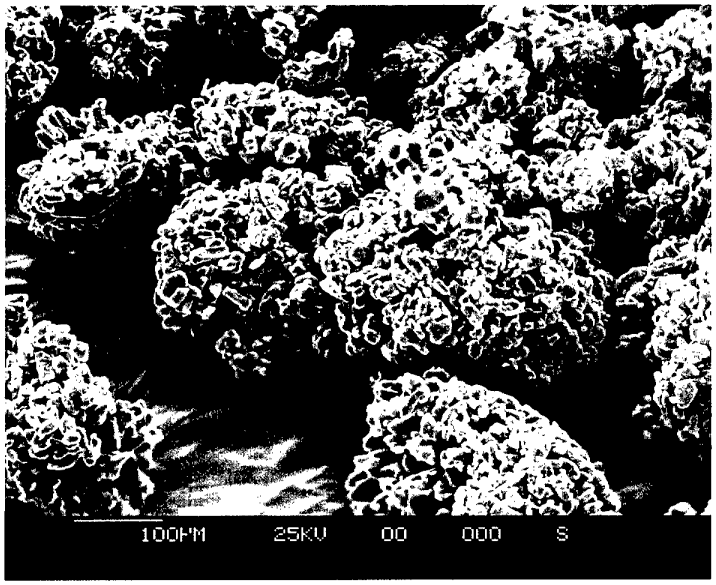


Figure 14. SEM Image of EVA coated FOX-7.

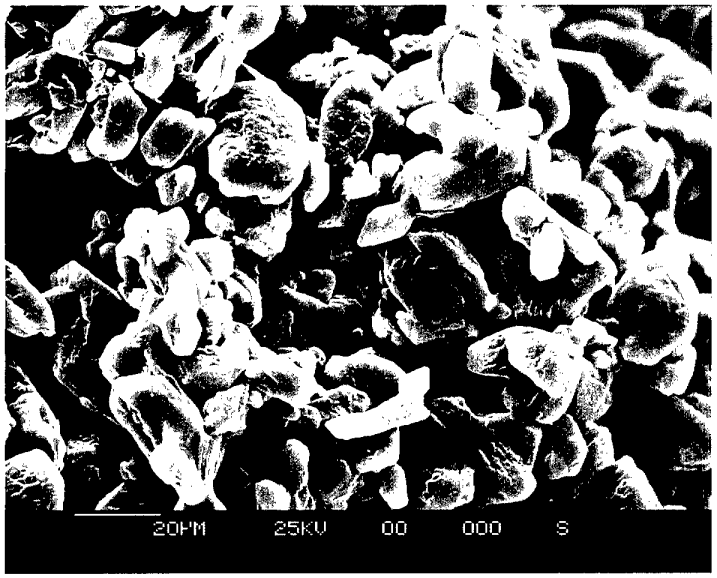


Figure 15. SEM Image of EVA coated FOX-7.

FOX-7/EVA pellets were produced by pressing a 2.5 g sample at a constant load of 20 kN. Nominal dimensions were 12.7 mm diameter x 12.0 mm and the average density

was 1.645 g/cm^3 (92% TMD). RDX/EVA pellets were produced at the same nominal size and % TMD.

Experimental detonation properties (Table 3) were determined from the following experiments. Twelve pellets of FOX-7/EVA were stacked to form a charge approximately 143 mm in length and 12.7 mm diameter. A pentolite donor was added and the complete charge was placed onto a 150 x 150 x 50 mm steel witness plate and detonated using an EBW detonator. The experiment was repeated in triplicate and parallel experiments with RDX/EVA were performed.

Velocity of detonation was determined from the digital streak record. Due to problems with the calibration software for the digital camera final velocity of detonation results are not yet available. The results presented are of the average velocity for the detonation front to travel through the length of the charge, not including the donor.

Relative detonation pressure was estimated from the dent depth in the witness plate relative to that created by the RDX/EVA charges.

4.1.1.3 Results

Table 3. Experimental and calculated performance parameters

		Experimental		Calculated[a]	
Explosive	**% TMD**	**VoD[b] (m/s)**	**P[c] (GPa)**	**VoD (m/s)**	**P (GPa)**
FOX-7	100			9090	36.6
RDX	100			8940	34.7
FOX-7/EVA	92	7730	24.1	7915	24.9
RDX/EVA[d]	92	7630		7731	23.0
FOX-7/EVA	100			8451	30.8
RDX/EVA	100			8232	28.1

[a] Cheetah v2.0
[b] tentative data
[c] average dent depth: FOX-7/EVA = 2.10, RDX/EVA = 2.00mm
[d] 94%/6%.

In summary, the limited experimental results validate the theoretical predictions that FOX-7 is slightly more powerful than RDX. The velocity of detonation of the FOX-7 charges is 100 m/s higher than the RDX charges and the detonation pressure shows a 5% increase. The experimental values are lower than those predicted by Cheetah however this difference is probably attributable to diameter effects. Also, as previously noted, the experimental velocities are only preliminary.

4.1.2 FOI Evaluation of the performance of FOX-7

No published experimental performance data for FOX-7 exist however information provided by FOI is that in a 25 mm cylinder test the velocity of detonation was 8870 m/s. No further details, such as charge density or the incorporation of binders, have been reported.

4.2 Discussion

RDX is regularly used as a benchmark for comparison with other explosive ingredients. With comparable performance and significantly improved sensitiveness, FOX-7 has obvious potential to be used as an explosive ingredient in IM formulation. Comparison with other insensitive ingredients such as NTO or TATB is also favourable, FOX-7 having significantly higher performance.

Table 4. Performance parameters for selected explosive compounds

	Calculated[a] Performance Parameters	
	Velocity of Detonation (m/s)	**Detonation Pressure (GPa)**
FOX-7	9090	36.6
RDX	8940	34.7
NTO	8564	31.2
TATB	8108	31.1

[a] Cheetah v2.0

5. Future Investigations

The synthesis of FOX-7 in-house at the DSTO laboratories is an inefficient use of resources and consequently sourcing FOX-7 from NEXPLO Bofors AB will be pursued as a high priority. With sufficient quantities of FOX-7 available, the major experimental focus is expected to be as follows.

Preliminary investigations into the modification of particle morphology and size will be continued, primarily via recrystallisation from dipolar aprotic solvents. Information from FOI is that further significant improvements in insensitivity can be made via this route.

Pressed charges of FOX-7/EVA (95:5) will be prepared as previously discussed for a variety of experiments including:

- Determination of velocity of detonation and detonation pressure for 25mm diameter unconfined charges. More accurate results will be sought through improved instrumentation along with a reduction in diameter effects compared with the initial experiments.

- Examination of the response to thermal stimuli via the super small-scale cookoff bomb [21].
- Determination of the relative shock sensitivity from the MRL small scale gap test [22].
- Determination of the Gurney energy by performing cylinder expansion tests.

In all cases parallel experiments with equivalent RDX/EVA charges will be performed.

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Helena Bergman from FOI has shared many ideas and results and her assistance is greatly appreciated. Thanks are due to Dr Jing Ping Lu for performing the Cheetah calculations and to Richard Dexter for sensitiveness testing and assistance with the experimental programme. Terminal Effects Group provided the instrumentation and firing support for the detonation experiments.

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Appendix A: Experimental Details

A.1. Synthetic Method

2-Methoxy-2-methyl-4,5-imidazolidinedione:

A 2 L round bottom flask was equipped with a magnetic stirrer bar, drying tube and a dropping funnel. The flask was charged with methanol (860 mL) and sodium methoxide (30 % in methanol, 232 mL). Acetamidine hydrochloride (36.48 g) was added to the stirred solution at room temperature to form a suspension. Diethyl oxalate (55.88 g) in methanol (400 mL) was added to the mixture over a period of 3 hours followed by stirring for an additional hour. The pH of the reaction was then adjusted to approximately 4 by the addition of concentrated hydrochloric acid at < 30 °C. The insoluble salts were removed by filtration through Filteraid (APS 1739) and the filtrate was evaporated to dryness at ≤ 30 °C to afford a white solid. This solid was added to 320 mL of boiling methanol and a hot filtration was performed to remove the insoluble salts. The total volume of the filtrate was then reduced to 320 mL. After cooling overnight in a refrigerator the resultant white crystalline product (35.5 g, 64 %) was collected by filtration and dried. NMR ^{1}H (DMSO-d_6) δ 1.58, s, 3H, CH_3; 2.98, s, 3H, OCH_3; 9.92, br s, 2H, NH. ^{13}C (DMSO-d_6) δ 26.85, 47.86, 91.59, 159.84.

2,2-Dinitromethylene-4,5-imidazolidinedione:

A 500 mL round bottom flask equipped with magnetic stirrer, thermometer, dropping funnel and drying tube was charged with concentrated sulphuric acid (198 mL) in an ice bath. 2-Methoxy-2-methyl-4,5-imidazolidinedione (35.4 g) was added slowly to the cooled acid solution, dissolving to form a clear yellow solution. Nitric acid (70 %, 43 mL) was added dropwise over 60 minutes at < 30 °C, the mixture changing from yellow to deep red and eventually to a pale orange suspension. This suspension was stirred at ambient temperature for 30 minutes. The crude product was collected by filtration and air dried before being used in the next step.

1,1-Diamino-2,2-dinitroethene:

The crude 2,2-dinitromethylene-4,5-imidazolidinedione was added to water (120 mL) in a 500 mL conical flask with stirring. The suspension was cooled to < 30 °C and aqueous ammonia (30 %) was added at a rate such that the temperature was maintained between 20 and 30 °C until pH 9 was reached. The resultant suspension was stirred at ambient temperature for 2 hours before the solid product was collected by filtration and washed with water (4 times). After air and vacuum drying (60 °C/7 mmHg) the bright yellow crystalline solid was identified as 1,1-diamino-2,2-

dinitroethene (19.66 g, 54.1 %). IR† (KBR) 3420, (NH_2), 3340, 3310 (NH_2), 3220 (NH_2), 1635 (NH_2), 1610, 1525 (NO_2), 1470, 1395, 1350 (NO_2), 1225, 1170, 1140, 1025, 750, 620, 520, 460 cm^{-1}. NMR ^1H (DMSO-d_6) δ 8.8, br s, 4H, NH. ^{13}C (DMSO-d_6) δ 128.3, 158.3.

A.2. Discussion

A.2.1 Scale-up

The production of the precursor 2-methoxy-2-methylimdazolidinedione has been scaled up to about 130 g at 45-55 % yield by performing the reaction in a 10 L beaker using high purity argon to exclude moisture.

No difficulties have been encountered when performing the nitration reaction at this scale (130 g precursor) however, as mentioned in chapter 2, the hydrolysis of the nitrated intermediate on this scale has resulted in a minor exotherm and frothing at pH 1.0 - 1.5. Attempts to eliminate this event have included reducing the time the nitrated intermediate is dried; increasing the volume of water; increasing the stirring rate to ensure a finely divided suspension of the nitrated intermediate; reducing the rate of addition of $NH_{3(aq)}$ - all were unsuccessful.

A.2.2 Improvements

Several ways to make the reaction simpler or more efficient have been investigated.

1) Performing the condensation reaction at higher concentration (33 % less methanol) resulted in reduced yields.
2) It has been reported [5] that hydrogen chloride gas can be used to acidify the precursor (**6**), thus avoiding the requirement for evaporating to dryness to remove the water. This was successfully performed in the DSTO laboratories however has no benefit for small scale synthesis
3) Removal of methanol from the crude reaction mixture at temperatures above 30 °C was attempted but resulted in significantly reduced yields
4) Nitration of the crude precursor, rather than recrystallised product, was attempted without success, presumably because of the presence of large quantities of sodium chloride.

† Infrared assignments from Latypov *et al* [5]

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19. ABSTRACT

1,1-Diamino-2,2-dinitroethene (FOX-7) is an energetic material developed by FOI Sweden in the late 1990s. Theoretical studies have predicted that the performance of FOX-7 should exceed that of RDX. FOX-7 is also significantly less sensitive than RDX, particularly to impact and frictions stimuli. Consequently, FOX-7 is an attractive ingredient for application in high performance, IM-compliant explosive compositions. AMRL evaluation of FOX-7 has focused on the synthesis, hazards characterisation and performance studies. Aspects of these research areas, including preliminary experimental data that validates the theoretical performance values, are detailed.

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