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Journal of Hazardous Materials B137 (2006) 812–819

Journal of Hazardous Materials

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Synthesis, characterization and thermolysis of 1,1-diamino-2,2-dinitroethylene (FOX-7) and its salts

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Received 26 January 2006; received in revised form 27 February 2006; accepted 1 March 2006
Available online 15 May 2006

Abstract

The present paper discusses the efforts made in HEMRL to establish the synthesis of FOX-7 at 100 g/batch level. In the present study, 1,1-diamino-2,2-dinitroethylene has been synthesised by treatment of acetamidinium chloride with diethylmalonate to obtain 2-methyl-pyrimidine-4,6-dione which on nitration followed by hydrolysis gave FOX-7. The synthesised FOX-7 has been characterized by spectroscopic and thermal techniques. The data obtained confirms the structure of FOX-7. The sensitivity of FOX-7 towards mechanical stimuli indicated its insensitive nature. The theoretically computed explosive and ballistic parameters are close to that of RDX. The synthesised FOX-7 has been used as a precursor for the synthesis of potassium and guanidinium salts and the thermal analysis of these salts indicate their exothermic nature.

Keywords: FOX-7; Potassium salt of FOX-7; Guanidinium salt of FOX-7; Insensitive high explosive; Synthesis; Characterization

1. Introduction

The quest for novel high energy materials (HEMs) with highest possible performance and low vulnerability led to the development of advanced insensitive power packed materials [1–3] such as triaminotrinitrobenzene (TATB), nitrotriazolone (NTO), dinitrotetraoxa diazatetracyclo dodecance (TEX) and 2,6-diamino-3,5-dinitropyrazine-*N*-oxide (LLM-105). Many of these insensitive HEMs are at various stages of pilot plant production in different countries. Eventhough these explosives are insensitive towards external stimuli, their performance is less than bench mark explosive RDX. Allover the globe research and development programs to develop insensitive HEMs with higher performance.

1,1-Diamino-2,2-dinitroethylene (FOX-7) is emerging as a potential candidate for its use in insensitive high explosive. The R&D work on FOX-7 is continuously pursued with great interest in many developed countries where the process has been scaled up to pilot plant level. Many research publications are appearing in the literature mentioning the potential of FOX-7 for insensitive applications. However, none of the processes discloses the actual processes parameters for the synthesis of FOX-7. In the light of these observations a research program on the development of process for the preparation of FOX-7 was embarked upon in HEMRL recently. Insensitive behavior of FOX-7 can be explained by its structure. The FOX-7 molecular geometry is characterized by extensive π conjugation, with two intramolecular hydrogen bonds between the nitro oxygen and the amino hydrogen atoms. The molecular arrangement inside the crystal is that of two-dimensional wave-shaped layers, with extensive intermolecular hydrogen bonding within the layers and with simple van der Waals interactions between the layers. Stresses inside the crystal are reduced by the movement of two layers, in this manner the crystal is getting more insensitive against mechanical strain. It has been suggested [4] that the molecular packing in FOX-7 is essential for its low sensitivity to impact and friction. The type of molecular packing in crystalline FOX-7 is similar to that observed in other relatively insensitive energetic materials such as TATB [5] and NTO [6]. 1,1-Diamino-2,2-dinitroethylene (FOX-7 or DADNE) has attracted substantial interest because it is expected that its sensitivity could be as low as that of TATB [7], and its performance comparable with the performance of RDX and HMX [8].

As Politzer et al. [9] have pointed out that this compound has the same molecular stoichiometric as RDX and HMX, which are among the most powerful currently used explosives and

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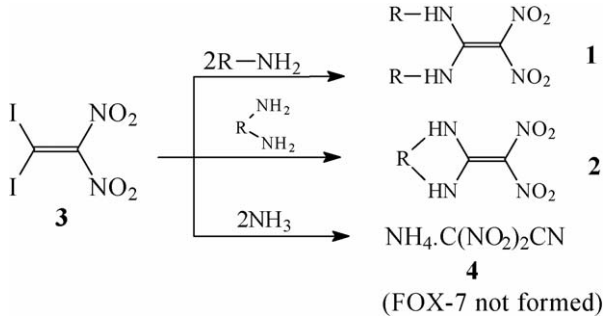
doi:10.1016/j.jhazmat.2006.03.034

monopropellants. Upon complete decomposition of all these molecules to CO, N_2 and H_2O, they would yield the same number of moles (0.0405) of gaseous product per gram of compound, one of the key determinants of explosive and propellant performance. It is interesting to note that the reported activation energy of decomposition (E_a = 58 kcal/mol for temperature interval 210–250) [10] for FOX-7 is higher than that of RDX (E_a = ~40 kcal/mol) [11–13] and HMX (E_a = ~35 kcal/mol) [14], which favors FOX-7 as an insensitive explosive. FOX-7 is a thermally stable insensitive high explosive with a performance very close to RDX [15]. The sensitivity of FOX-7 to physical stresses such as impact, friction, heat etc. has been extensively studied [16,17]. These studies support the belief that FOX-7 is a prime candidate as a energetic filler in insensitive munitions.

FOX-7 was first synthesised in 1998 by Latypov et al. [18] since then different synthetic methods have been developed and FOX-7 is now synthesised in a pilot plant on a multi-kilogram scale in NEXPLO Bofors, Sweden. Earlier, Baum et al. [19] synthesised several 1,1-bis-(alkylamino)-2,2-dinitroethylenes (**1**, **2**, Scheme 1) by reacting 1,1-diiodo-2,2-dinitroethylenes (**3**, DIDNE) with alkyl amines, but when DIDNE was reacted with ammonia FOX-7 was not formed, the major product was identified as ammonium cyanodinitromethide, **4** ($NH_4{\cdot}C(NO_2)_2CN$).

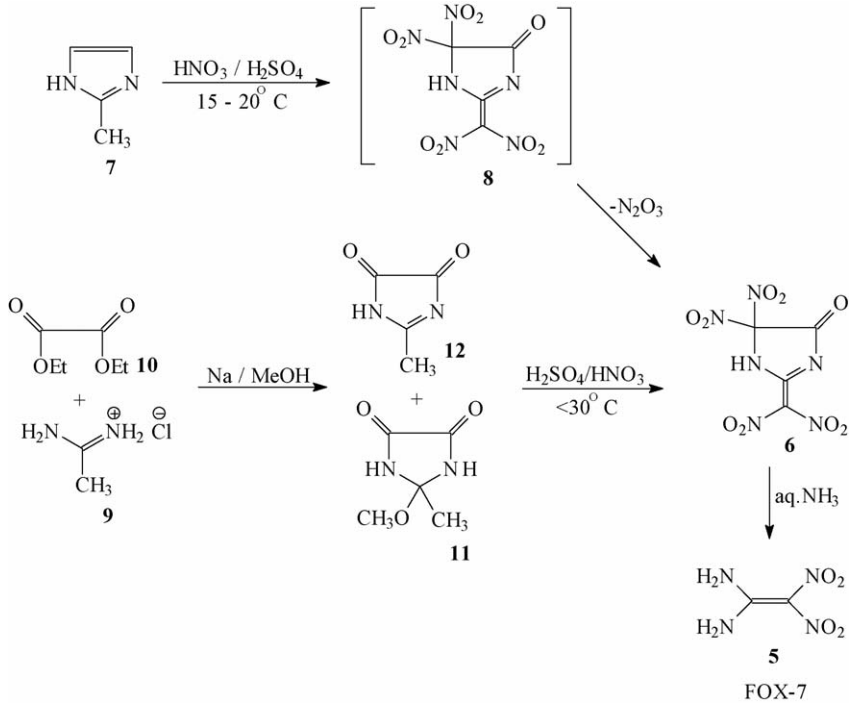
FOX-7 (**5**, Scheme 2) is prepared by the hydrolysis of 2-(dinitromethylene)-4,5-imidazolidinedione (**6**) with aqueous ammonia. Compound **6** may be prepared by two basic methods [18]. *Method 1*: The nitration of 2-methylimidazol (**7**) with mixed acid produces postulated intermediate 2-dinitromethylene-4,4-dinitro-5-imidazolidinone, (**8**) which decomposed at room temperature to give the compound (**6**). This method was found to be very important to control the



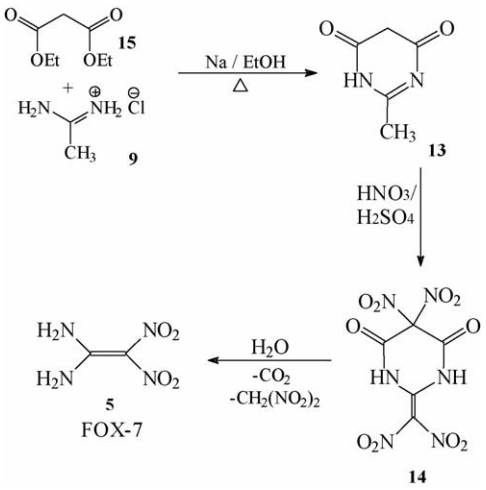
Scheme 1.

temperature of the nitration reaction. The product was isolated as a solid in low yield (<15%). *Method 2*: The reaction of acetamidine hydrochloride (**9**) with diethyl oxalate (**10**) provides the mixture of 2-methoxy-2-methyl-4,5-imidazolidinedione (**11**) and 2-methyl-4,5-imidazolidinedione (**12**). This product mixture **11** and **12** or **11** alone are nitrated by mixed acid to from 2-(dinitromethylene)-4,5-imidazolidinedione (**6**). *Method 3*: The synthetic route to FOX-7 is based (Scheme 3) upon the nitration of 4,6-dihydroxy-2-methylpyrimidine (**13**) in mixed acid at low temperature. This reaction leads to the precipitation of 2-dinitromethyleme-5,5-dinitrodihydropyrimidine-4,6-dione (**14**) which is easily hydrolyzed in water to FOX-7 and dinitromethane. The starting material is prepared from acetamidine hydrochloride (**9**) and diethylmalonate (**15**) in the presence of sodium in ethanol. However, in contrast to compound **11** it is easily isolated and purified for further nitration.

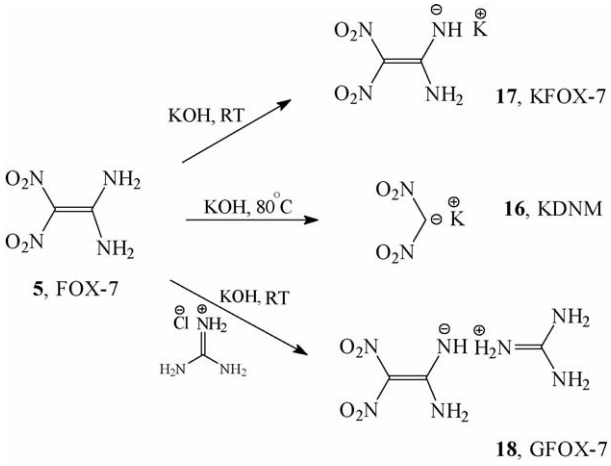
Dinitromethane (DNM) salts, suitable as intermediates and starting material for production of explosives and propellants.



Scheme 2.



Scheme 3.



Scheme 5.

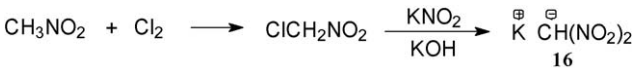
Potassium dinitromethane was first prepared by Villiers [20] in 1884 by reduction of bromodinitromethane, which was obtained [21] in low yield. Free dinitromethane [22] unstable pale yellow oil, decomposes readily at ambient temperature. Dinitromethane salts are obtained from the alkali salts of dinitroethylene by oxidative nitration of nitroethanol. Dinitromethane is also reported to be prepared by nitration of halogenated olefins, such as trichloroethylene. Potassium dinitromethane (**16**) was prepared [23,24] from chloronitromethane (Scheme 4).

However, all those methods provide low yields of dinitromethane salts but involve drastic reaction conditions and inconvenient methods and isolation of end product. The present investigation resulted to a more practical synthesis of dinitromethane salts. New routes to the potassium dinitromethane (KDNM, **16**) is based on hydrolytic ring cleavage of 2-dinitromethyleme-5,5-dinitrodihydropyrimidine-4,6-dione (**14**) as a result formation of dinitromethane, followed by conversion of it to potassium salt by treating with KOH in diethyl ether in good yield.

Furthermore, this paper reports the synthesis, characterization and thermal studies of potassium and guanidinium-based FOX-7 salts by the treatment of potassium hydroxide or quanidinium hydrochloride with FOX-7 in water or FOX-7 in potassium hydroxide solution, respectively. FOX-7 is a nitroenamine belonging to the group of compounds known as push–pull alkenes [25] which possesses a highly polarized carbon–carbon double bond, with positive and negative charges being stabilized by the two amino groups and the two nitro groups, respectively. Therefore, FOX-7 is expected to form salts with alkaline metals and quaternary organic bases.

Potassium salt of FOX-7 (KFOX-7, **17**) was prepared by the addition KOH solution to FOX-7 suspended in water at room temperature. When this mixture was heated at 80 °C it produce pale yellow colored potassium dinitromethane (**16**). Similarly, guanidinium salt of FOX-7 (GFOX-7, **18**) was prepared by the addition of guanidinium hydrochloride solution to FOX-7 in KOH solution (Scheme 5).

FOX-7 has interesting properties as a high explosive and has also application in the synthesis of nitrogen heterocycles. The compound is also special for its good insensitivity on one hand and high performance on the other hand. Thus, this compound is a potential candidate for of LOVA (low vulnerability ammunition) [16].



Scheme 4.

2. Materials and methods

2.1. Materials

AR grade chemicals and absolute ethanol were used in this process without further purification. Melting points were determined in an open capillary and are uncorrected. The UV spectrum (Jasco-V 530) of the compound has been recorded in acetonitrile. The IR spectra (FTIR-1600 spectrophotometer) were recorded on a Perkin-Elmer using KBr matrix. The DSC studies was carried out on a Perkin-Elmer DSC-7 instrument operating at a heating rate of 10 °C/min in nitrogen atmosphere and the mass of the sample used was less than 1 mg. ^{1}H NMR (Varian 300 MHz) spectrum of FOX-7 was recorded in deuterated chloroform at 30 °C with TMS as an internal standard. The thermal properties of DADNE were studied by simultaneous thermogravimetry (TG)/differential thermal analysis (DTA) (Mettler Toledo Star System). The sensitivity to impact of FOX-7 was determined by using a 2-kg drop weight and the results are reported in terms of height for 50% probability of explosion. Figure of insensitivity (F of I) was computed by using tetryl (Composition Exploding, CE), as reference. The friction sensitivity of the compound was determined using a Julius Peter's apparatus till there was no explosion/ignition in five consecutive test samples at that weight. The results obtained for impact and friction were within the uncertainty limits of ±5 cm and ±0.2 kg, respectively.

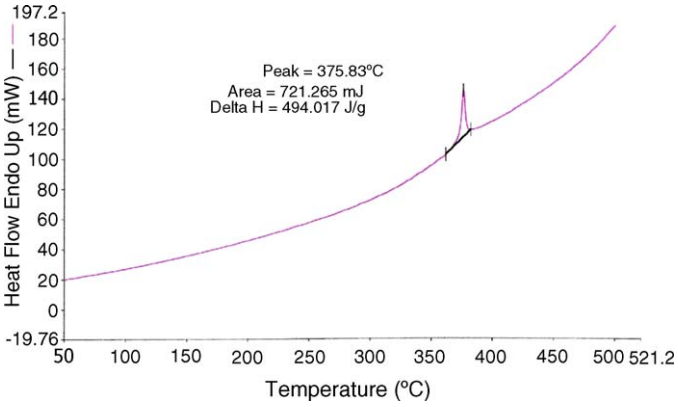


Fig. 1. DSC profile of 4,6-dihydroxy-2-methylpyrimidine.

2.2. Experimental

2.2.1. Preparation of 4,6-dihydroxy-2-methylpyrimidine (*13*)

7.2 g of sodium was dissolved in 200 ml of cold absolute ethanol (99.9%) in 500 ml RB flask equipped with thermometer and water condenser (dissolution of sodium in ethanol heat will be generated therefore, the content was kept under ice-cooling). 14.2 g of acetamidinium chloride was added into above solution and the mixture was stirred at room temperature. After 15 min, 22.8 ml of diethyl malonate was added into the reaction mixture at room temperature. The resulting mixture was stirred at 90 °C for 5–6 h. After completion of reaction it was cooled to room temperature, the white precipitate was collected by filtration (The solid contain mixture of 4,6-dihydroxy-2-methylpyrimidine and sodium chloride) which was dissolved in ice-cold water ~400 ml and then it was acidified to pH 2 by adding concentrated hydrochloric acid (~10 ml) under ice-cold condition, a white precipitate was formed. The formed precipitate was separated by filtration (the aqueous filtrate contains sodium chloride) and washed with water and ethanol to give white solid mass, which was dried in oven at 90 °C for 1 day to give 12.3 g (65% yield based on acetamidinium chloride) of 4,6-dihydroxy-2-methylpyrimidine (**13**). Melting point (DSC): 376 °C (Fig. 1); IR (KBr): 1687, 1641, 1577, 1456, 1329, 533, 525 cm^{-1}; ^1H NMR (DMSO-D_6): δ 4.95 (s, 1H), 2.21 (s, 3H); Elemental analysis (%): Calculated for $C_5H_6N_2O_2$: C, 47.62; H, 4.80; N, 22.21; Found: 46.61; H, 4.40; N, 23.21.

2.2.2. Preparation of 1,1-diamino-2,2-dinitroethylene (*5*, FOX-7)

4,6-Dihydroxy-2-methylpyrimidine 14.5 g was dissolved in 60 ml of 98% sulphuric acid at room temperature and the mixture was cooled in water bath to 4–8 °C. 23.6 ml of fuming nitric acid was then added drop-wise for 15 min. The temperature of the reaction mixture was kept below 10 °C during this addition. The reaction mixture was then allowed to attain room temperature and after 3 h the reaction mixture was transferred to a mixture of ice and water under stirring. The precipitate got dissolved completely with CO_2 evaluation, and then bright yellow crystals of 1,1-diamino-2,2-dinitroethylene precipitated after 1 h. This precipitate was filtered-off and was washed with water and dried to give 13.5 g (82.12%) of FOX-7. IR (KBr): 3408 (NH_2), 3330 (NH_2), 1636 (NH_2), 1520 (NO_2), 1472 (NO_2) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.64 (brs, 4H, $2NH_2$); ^{13}C NMR (DMSO-d_6): δ 128.1, 158.3; Anal. Calcd. for $C_2H_4N_4O_4$: C, 16.22; H, 2.72; N, 37.84%; Found: C, 16.12; H, 2.79; N, 37.75%. The obtained data were compared with literature values [18]. The filtrate was extracted with diethyl ether (3 ml × 60 ml). The ether phase was added to a solution consisting of potassium hydroxide (6 g) in 100 ml of ethanol and the solution was cooled to 0 °C. Potassium dinitromethane then precipitated, was filtered off and recrystallized in 100 ml of water. Yield 10.8 g of KDNM (**16**).

2.2.3. Preparation of potassium dinitromethane from FOX-7 (*16*)

Potassium dinitromethane also can be prepared from alkaline hydrolysis 1,1-diamino-2,2-dinitro ethylene (Scheme 5). FOX-7 (2.96 g, 20 mmol) was dissolved in a solution of 5.9 g KOH in 50 ml of water; the resulting solution was warmed up to 80 °C and was kept at this temperature 3 h until evolution of ammonia ceased. After that the solution was cooled to 0 °C temperature and the pale yellow product **16** (Scheme 5) formed was collected by filtration, washed with water and dried. All spectral and thermal characteristics of the product were identical with those of potassium dinitromethane; yield 2.51 g (87%).

2.2.4. Preparation of KFOX-7 (*17*)

FOX-7 (1.48 g, 10 mmol) was suspended in 8 ml of water and to it a solution of KOH (1.2 g in 2.0 ml of water) was added drop wise. The solution formed was diluted with 30 ml methanol. The resulting suspension was filtered off, washed with methanol (2 ml × 5 ml) and dried at 40 °C. 1.69 g (91%) of KFOX-7 ($0.5H_2O$) was obtained as a hemi-hydrate (Scheme 5).

2.2.5. Preparation of GFOX-7 (*18*)

FOX-7 (1.48 g, 10 mmol) was suspended in 8 ml of water and to it a solution of KOH (1.2 g in 2.0 ml of water) was added drop wise. After complete dissolution, guanidinium chloride solution was added and the resulting mixture was cooled to 0 °C (Scheme 5). Yellow color crystals of GFOX-7 was formed which was filtered and dried under vacuum, yield 1.98 g (95%).

3. Results and discussion

3.1. Solubility of FOX-7

FOX-7 is a bright yellow crystalline powder. The product isolated directly from the above reaction is typically of high purity with a particle size of the order of 5–15 μm and density of FOX-7 is 1.88 g/cm^3 (crystal density). FOX-7 is only slightly soluble in common organic solvents and water but readily dissolves in dipolar aprotic solvents such as dimethyl sulfoxide, *N*,*N*-dimethyl formamide and 1-methyl-2-pyrrolidinone.

3.2. Spectral studies

The purity FOX-7 was found out to be higher than 99.6%. The UV spectrum of FOX-7 indicates the following absorbance: a stronger band at 215.95 nm (for normal carbon–carbon double bond: 165 nm) for $\pi \rightarrow \pi^*$ transition corresponds to ethylene carbon–carbon double bond (C=C). The higher value clearly indicates that the presence of extensive π conjugation in the molecule and a stronger band at 279 nm for $n \rightarrow \pi^*$ transition due to the presence of nitro groups. The IR spectrum of FOX-7 showed the presence of primary amino groups at 3408, 3330, 1636 cm^{-1} and nitro groups at 1520, 1472 cm^{-1} in the molecule. ^1H NMR spectrum of the FOX-7 sample showed a single broadened signal of four hydrogen atoms of two amino groups with the chemical shift δ 8.64 ppm. ^{13}C NMR spectra showed two signals, a signal of carbon attached with amino group at 128.1 ppm and a signal of carbon attached with nitro group at 158.3 ppm.

The IR spectrum of KFOX-7 reveals stretching vibration frequencies at 3399, 3315 (NH_2), 1655 and 1551 cm^{-1} for carbon–carbon double bond and nitro groups, respectively. The IR spectrum of GFOX-7 shows stretching vibration frequencies at 3433, 3343, 3288 (NH_2 and NH), 1654, 1588, 1477 (C=C and NO_2) cm^{-1}. The melting point of dinitromethane (DNM) was measured by open capillary and it detonates at 128 °C. The IR spectrum of DNM shows the peaks at 3146, 1462, 1428 cm^{-1} (C–H, NO_2).

3.3. Thermal and sensitivity studies

The DSC thermogram of FOX-7 indicates two decomposition steps with peak maxima (T_{max}) at 240.10 °C ($\Delta = -473$ J/g) and 279.43 °C ($\Delta = -542$ J/g). The spark sensitivity test of FOX-7 results indicates no ignition for five consecutive tests, at spark gap energy of 5 J (10 kV, 30 °C, 55% RH). The DSC profile of KFOX-7 (Fig. 2) reveals an exothermic decomposition at 225 °C (T_{max}, $\Delta H = -386$ J/g), whereas DSC profile of GFOX-7 (Fig. 3) shows three peaks. The first endothermic peak at 200 °C (T_{max}, $\Delta H = 260$ J/g), second and third exothermic peak at 208 °C (T_{max}, $\Delta H = -705$ J/g) and 283 °C (T_{max}, $\Delta H = -1279$ J/g), respectively. The impact ($h_{50\%}$ 34 cm) and friction (16 kg) sensitivity of KFOX-7 indicates its sensitivity nature towards mechanical stimuli. Whereas sensitive data obtained for GFOX-7 clearly shows that GFOX-7 is very insensitive towards impact and friction ($h_{20\%}$ 170 cm and >36 kg).

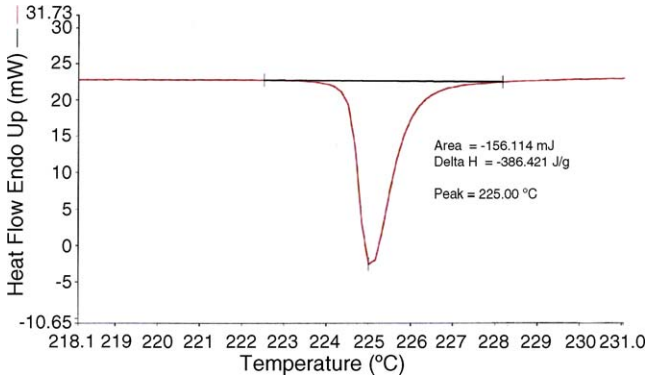


Fig. 2. DSC profile of KFOX-7.

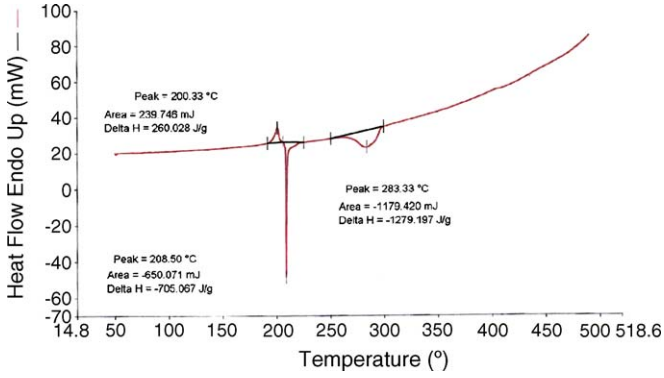


Fig. 3. DSC profile of GFOX-7.

3.4. SEM studies

The surface morphology studies of FOX-7 by SEM image showed that FOX-7 (Fig. 4(a) and (b)) has cubic/rod type crystal morphology. The average particle length and width of FOX-7 crystals is 49 and 6.5 μm, respectively. The SEM results showed that KFOX-7 and GFOX-7 (Figs. 5 and 6) has plate/cubic and cubic rod shaped crystal morphology, respectively, whereas KDNM has cubic shaped morphology (Fig. 7).

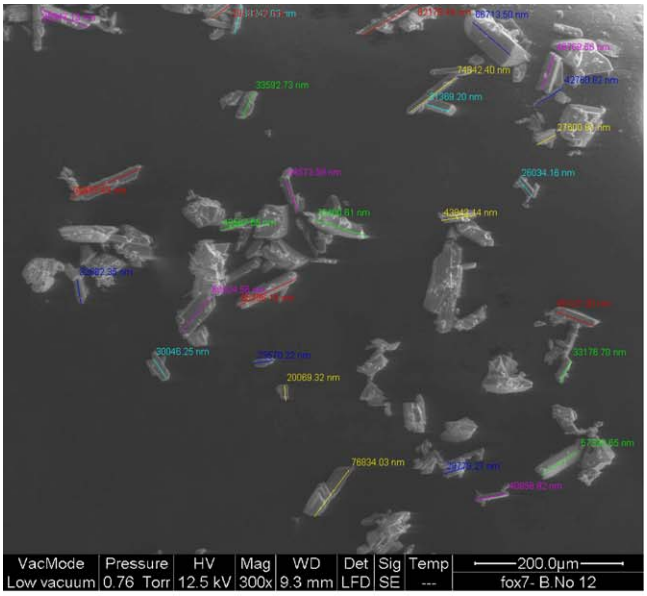
3.5. Explosive properties of FOX-7 and comparison with RDX, TEX and TATB

The results (Table 1) of the explosive characterization shows that FOX-7 is thermally quite stable and in almost all situations is significantly less sensitive then the benchmark RDX. The results for impact and friction sensitiveness clearly demonstrate

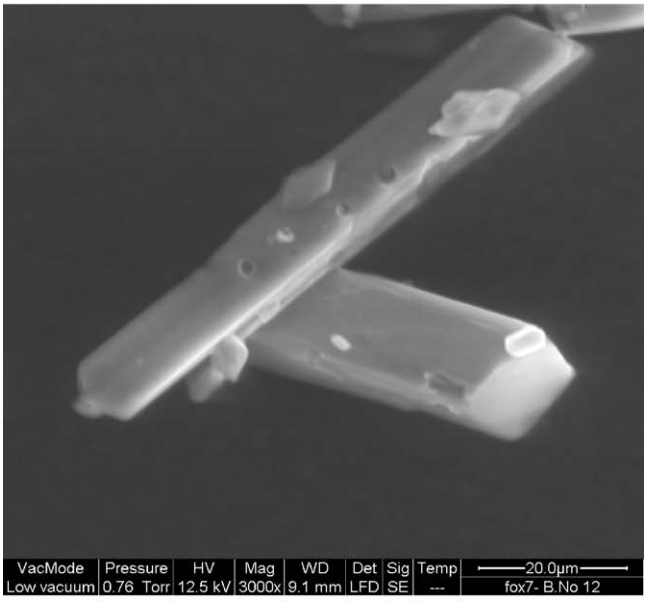
Table 1
Explosive properties of FOX-7 in comparison with RDX, TEX and TATB

S. no.	Properties	FOX-7	RDX	TEX	TATB
1	Detonation velocity (m/s)[a]	9090	8800	8749	8108
2	Detonation pressure (GPa)[a]	36.6	34.7	36.5	31.1
3	Drop weight test (cm)	126	38	177	170
4	Friction test (kg)	>36	12	>36	>36
5	Thermal stability (°C)	240	215	285	287

[a] Calculated values by Cheetah v 2.0.



(a)



(b)

Fig. 4. SEM image of FOX-7 crystals.

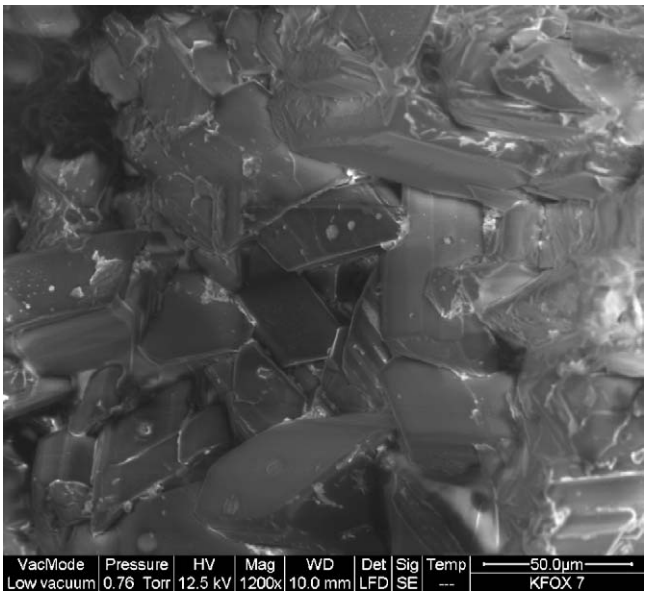


Fig. 5. SEM image of KFOX-7 crystals.

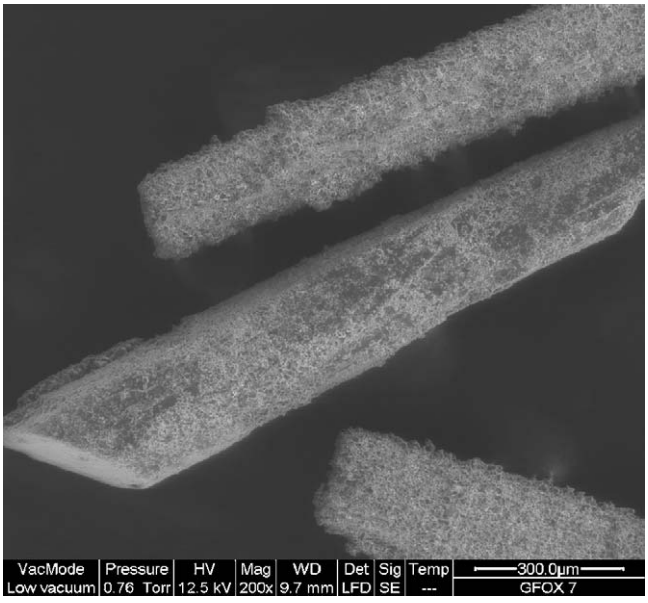


Fig. 6. SEM image of GFOX-7 crystals.

Table 2
Predicted performance parameter of FOX-7-based formulation

Entry	Composition (%)					Calculated values			
	SNC	CL	Al	FOX-7	RDX	T_f (K)	MM[a] (wt.)	C (m/s)	I_{sp}
1	–	–	–	–	100	3282	24.7	1645	265.4
2	–	–	–	100	–	2799	24.7	1491	239.1
3	30	40	–	–	30	2782	24.1	1504	241.2
4	30	40	–	30	–	2603	24.1	1450	232.6
5	20	40	–	–	40	2887	24.2	1532	245.8
6	20	40	–	40	–	2655	24.8	1463	234.6
7	29	36	17.5	–	17.5	3536	29.0	1595	263.5
8	29	36	17.5	17.5	–	3470	29.1	1574	260.2

[a] Mean molecular weight.

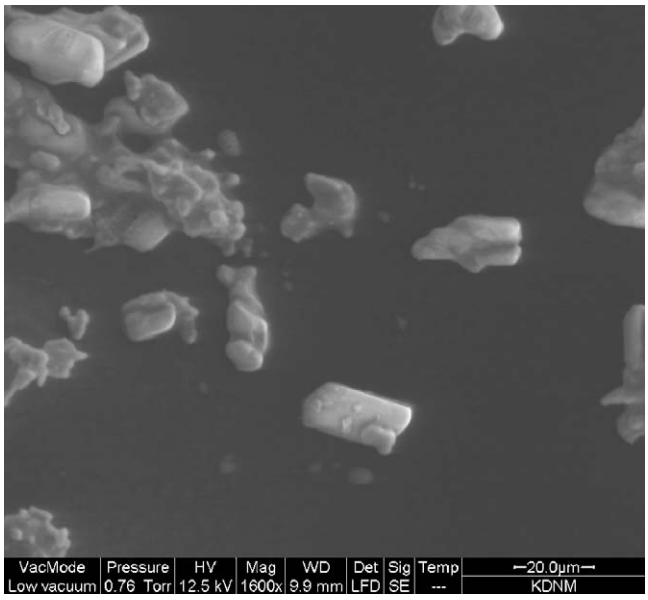


Fig. 7. SEM image of KDNM crystals.

the promise of FOX-7 as an insensitive ingredient for explosive and propellant formulations.

3.6. FOX-7-based propellant formulation

The explosive and ballistic parameters were predicted using molecular formula, density and heat of formation data. The ballistic parameters, such as specific impulse (I_{sp}), mean molecular weight of exhaust gases, flame temperature (T_f), etc. were computed using NASA programme [26]. Explosive and ballistic parameters of FOX-7 and FOX-7 containing formulations are presented in Table 2. The predicted ballistic parameters of FOX-7 incorporated double-base propellant formulations show that I_{sp} and characteristic velocity are comparable with RDX incorporated double-base propellants. Whereas the results obtained from aluminium incorporated FOX-7 containing double-base propellants are very close to aluminium incorporated RDX double-base propellants (Table 1, entry 7 and 8)

4. Conclusion

FOX-7 has been successfully synthesised during this work. Spectral and sensitivity data obtained for the synthesised product are in line with the results reported by other researchers. A feasibility study on scale up of FOX-7 at 100 g/batch level was established. The by product dinitromethane which is formed during hydrolytic ring cleavage of 2-dinitromethyleme-5,5-dinitrodihydropyrimidine-4,6-dione can be isolated and could be used as key intermediate for preparation of many energetic materials. FOX-7 has been used as a precursor for the synthesis of potassium and guanidinium salts and the thermal analysis of these salts indicate their exothermic nature. Potential of FOX-7 as an energetic ingredient in place of RDX in nitramine double base propellant was also studied. Ballistic and explosive parameters of FXO-7 and FOX-7 containing propellant formulations have been computed which suggest their performance comparable with the RDX incorporated propellant formulations and further work in this direction is in progress.

Acknowledgement

Authors are grateful to Director, HEMRL for his encouragement and valuable suggestions in this work.

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