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N-guanylurea-dinitramide: a new energetic material with low sensitivity for propellants and explosives applications

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Abstract

FOX-12, or *N*-guanylurea-dinitramide, is a novel energetic material with low sensitivity and good potential for use as a propellant or insensitive munitions (IM) explosive. This paper reports its synthesis, sensitivity (friction and drop weight), thermal stability and explosion temperature, as well as its bulk crystal density, $\rho = 1.7545$ g/cm^3 (powder X-ray), and its heat of formation, $\Delta H_f^\circ = -355$ kJ/mol (bomb calorimetry). The activation energy ($E_a = 277$ kJ/mol) was measured with a differential scanning calorimeter (DSC). The ignition temperature was measured using Wood's metal bath ($T_{ign} = 192$ °C). Using a thermo-chemical code (Cheetah 1.40) and the experimentally determined values of density and heat of formation, the performance was estimated.

Keywords: Energetic materials; DSC; X-ray; Raman; Explosives; Dinitramide; FOX-12

1. Introduction

Since the recently published synthesis of the new nitrogen oxy-anion dinitramide [1], a large number of papers on dinitramide salts have been published. Of this new class of energetic materials, the most well known is ammonium dinitramide (ADN) on which a large number of papers have been published (e.g. [2–7]). A number of other metal and organic ion salts (e.g. Li, K, Cs and biguanidinium) have also been studied [1,6,8–11]. Most of these salts are water soluble and highly hygroscopic. We present here a new dinitramide salt, FOX-12 or *N*-guanylurea-dinitramide, see Fig. 1, which is neither soluble in cold water nor hygroscopic, and has a very low sensitivity. This paper presents basic properties (heat of formation, crystal density) and sensitivity (friction, impact and DSC) data. The paper presents some initial performance calculations of FOX-12 for use as an IM explosive, gun and rocket propellant (thermo-chemical calculations of detonation velocity, detonation pressure, impetus and specific impulse). It also presents some spectroscopic properties of FOX-12 (Raman). The paper also explains the relatively large thermal and impact insensitivity of FOX-12, based on its crystal structure.

2. Synthesis

The FOX-12 used for this work was synthesized using the following procedure: guanylurea sulfate hydrate (3.2 g, 0.01 mol) was dissolved in water (15 ml) and the pH was adjusted to 5–7 by dripping diluted sulfuric acid into the water. Thereby a clear solution was obtained. Ammonium dinitramide (2.5 g, 0.02 mol) was dissolved in water (3 ml). The two solutions were combined and a precipitate was formed. The precipitate was collected and washed

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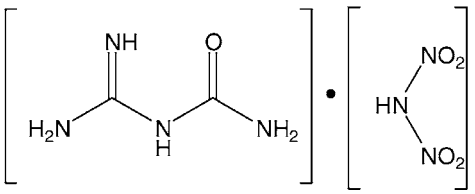

Fig. 1. FOX-12 (*N*-guanylurea-dinitramide).

with cold water and after drying guanylurea-dinitramide (3.4 g, 0.016 mol, 81%) was obtained as fine white crystals. Elemental analysis of the product agrees well with calculated values: carbon 11.6% (11.5%), nitrogen 47.0% (46.9%) and hydrogen 3.4% (3.4%). Values within parenthesis are calculated mass percentages for FOX-12. Identification of the substance was done by FT-IR, FT-Raman and X-ray analysis (see below). The crystal density was measured using powder X-ray diffraction and found to be $\rho = 1.7545(4)$ g/cm^3. A manuscript with the full single-crystal X-ray diffraction investigation and ab initio quantum mechanical calculations is under preparation [12]. The heat of formation (ΔH_f°) for FOX-12 was calculated from a measured heat of combustion. The apparatus used for the experimental determination was an adiabatic bomb calorimeter of the IKA C 4000 type. The calibration of the calorimeter was done by combustion of certified benzoic acid in oxygen atmosphere at a pressure of 3 MPa. The heat of formation was determined to be −355 kJ/mol.

Table 1
Sensitivity data for FOX-12 in comparison with ADN and RDX

Explosive	Drop height (cm)	Friction test (N m)	Comments
FOX-12	>159	>350	Raw FOX-12
ADN	31	>350	Un-prilled material [7]
RDX	38	120	

3. Sensitivity

Both impact and friction sensitivity were measured for FOX-12. The impact sensitivity was measured using a BAM apparatus [13] with a 2 kg drop weight, while the friction sensitivity was measured with a Julius–Petri friction apparatus [13]. The results for both types of sensitivity are based on tests on both sides of the 50% probability level using an up-and-down method. The results from these measurements can be found in Table 1 where data for RDX and ADN are given for comparison. As can be seen FOX-12 is very insensitive, it has a lower sensitivity than ADN although it has a higher predicted detonation performance.

4. DSC and ignition temperature measurements

The basic thermal stability of FOX-12 was measured with DSC using a Mettler 30 instrument. A typical DSC curve is shown in Fig. 2. The samples were heated

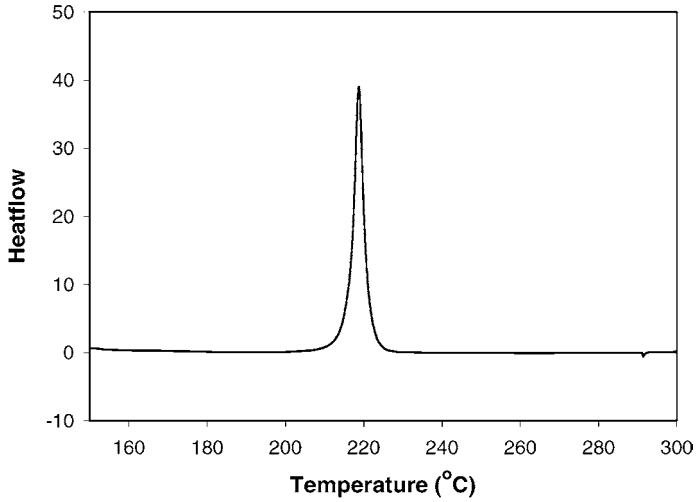

Fig. 2. DSC curve for FOX-12 at 7°/min.

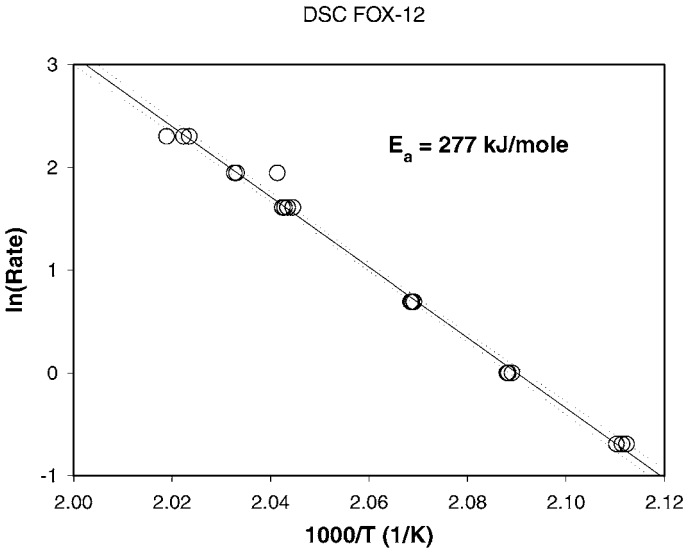

Fig. 3. DSC plot of ln(heating rate) vs. $1/T$ at maximum isotherm for FOX-12.

from room temperature with a heating rate of 0.5–10 °C/min. FOX-12 has an onset at 214.8 °C with a heating rate of 10 °C/min. Fig. 3 shows a plot of ln(heating rate) vs. $1/T$ at maximum isotherm. Using these data and the ASTM method E 698–79, the activation energy (E_a) was measured (temperature interval 200–225 °C), see Table 2. Compared to both RDX [14] and ADN [7], FOX-12 has larger activation energy indicating a high degree of thermal stability.

The sensitivity to thermal ignition was measured using the Wood's metal bath technique [13]. The ignition temperature was found to be 192 °C. Data from these measurements is shown in Fig. 4. The ignition temperature measured for FOX-12 is slightly lower than that of RDX ($T_{ign} = 210$ °C) but higher than that of ADN, which has an ignition temperature of 160 °C [7]. The ignition temperature measured for FOX-12 is relatively low; RDX tested in the same apparatus under the same conditions gave a temperature of ignition at 210 °C. From these measurements the activation energy was also determined, $E_a = 149$ kJ/mol, see Fig. 5. This value differs from that measured by DSC by a large number, indicating that FOX-12 has a higher reaction order or a different decomposition mechanism in these experiments than in the DSC measurements. Thermogravimetric measurements gave an onset of 209 °C; see Fig. 6. The increased thermal stability, compared with ADN, shows that the dinitramide ion can be stabilized by hydrogen bonding [15] and is not intrinsically unstable as was believed earlier. This is encouraging, as it seems likely that other low sensitivity dinitramide salts can be synthesized.

Table 2
Kinetic parameters from thermal experiments on FOX-12

Explosive	E_a (kJ/mol)	$\log(K_0)$ (s^{-1})	Temperature interval (°C)	Comments
FOX-12 (DSC)	277	29.4	200–225	
FOX-12 (Wood)	149	–	190–240	
ADN (DSC)	158	15.8		
ADN (Wood)	127	–		
RDX (DSC)	201.5	18.8		[14]

5. FT-IR and FT-Raman spectroscopy

FT-IR spectroscopy is normally used for the routine identification of ADN. Recently, FT-Raman spectroscopy has emerged as an interesting complement or alternative to FT-IR in explosives analysis [16,17]. This method uses only a small amount of solid sample (a few milligram of powder) and is very easy to perform. Fig. 7 shows an FT-Raman spectrum of FOX-12. The FT-Raman spectrum presented here was measured with a Brucker IFS 55 equipped with a Raman attachment. The excitation wavelength was

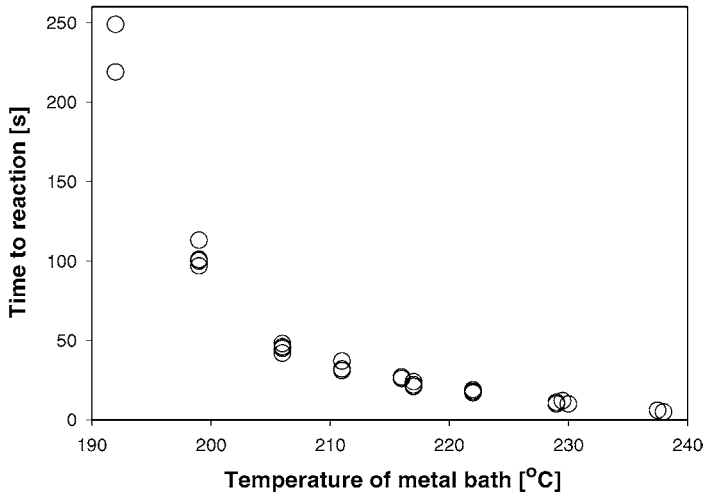

Fig. 4. Time to ignition vs. temperature for FOX-12 measured using Wood's metal bath.

1064 μm and the resolution used was 4 cm^{-1}. The conclusion from the FT-Raman measurements is that FT-Raman gives a sharper peak and is easier to interpret than the corresponding IR spectrum.

6. Performance

The heat of formation for FOX-12 was both calculated and measured. The apparatus used for the experimental determination was an adiabatic bomb calorimeter of the IKA C 4000 type. The calibration of the calorimeter was done by combustion of certified benzoic acid in oxygen atmosphere at a pressure of 3 MPa. The heat of formation was experimentally determined to be −355 kJ/mol. The calculated heat of formation, using MOPAC 6.0 [18–20] and the *PM3* parameter set, was $\Delta H_f^\circ = -155$ kJ/mol from which the correction for the heat of sublimation for FOX-12 (estimated value) has to be subtracted. This is far from the experimentally determined value of the heat of formation and this difference is probably due to extensive

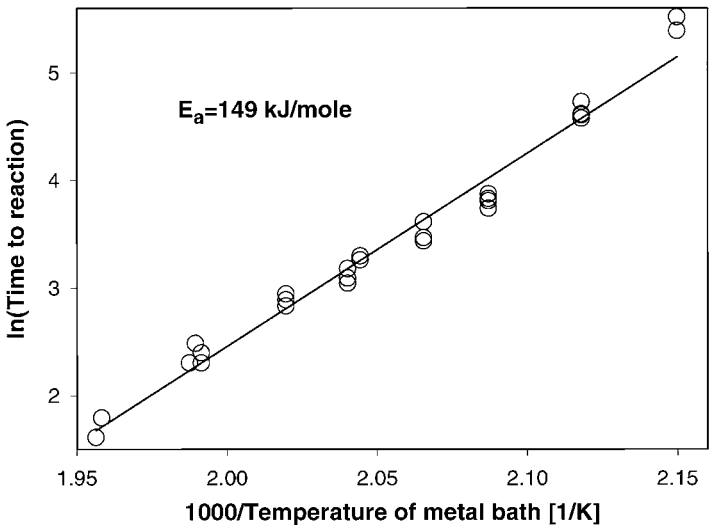

Fig. 5. Arrhenius plot of Wood's metal bath data for FOX-12.

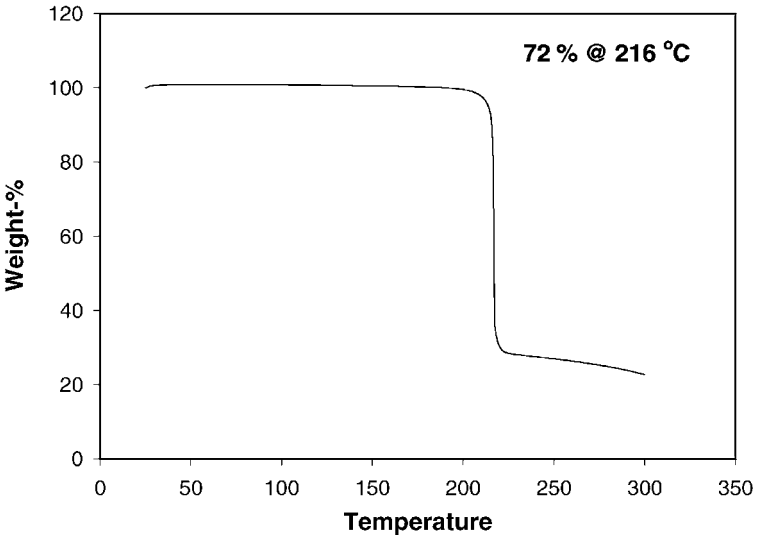

Fig. 6. TG curve of FOX-12.

hydrogen bonding. The density of FOX-12 was determined by powder X-ray diffraction and was found to be 1.7545 g/cm^3. The performance of FOX-12 for us in a number of different applications was estimated by thermo-chemical calculations using the Cheetah 1.40 [21] computer code. These calculations were based on the measured powder diffraction density ($\rho =$ 1.7545 g/cm^3) and heat of formation ($\Delta H_f^\circ = -355$ kJ/mol). The results are shown in Table 3.

7. Burn properties

Since FOX-12 can be used as a monopropellant it is of great interest to know the burn rate as a function of pressure. This was measured using a ballistic bomb and the result is shown in Fig. 8. The burn rate exponent, n, for FOX-12 is 0.73. NC-propellant under the same condition has a burn rate exponent of $\sim$0.9.

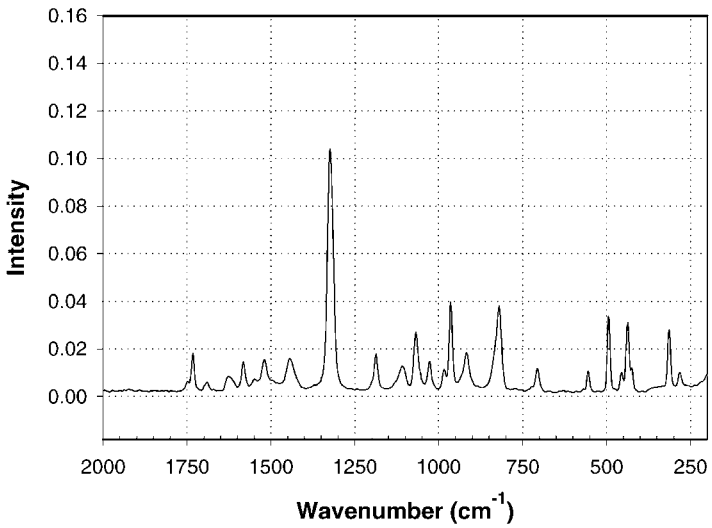

Fig. 7. FT-Raman spectrum of FOX-12.

Table 3
Calculated performance of FOX-12

	Calculated performance[a]		Calculated gun propellant performance[b]		Calculated rocket propellant performance[c]
	Detonation velocity (m/s)	Detonation pressure (GPa)	Impetus (J/g)	Temperature (K)	Specific impulse (s)
FOX-12	8210	25.7	953	2680	213.1
TNT	6900	19.4			
RDX	8900	34.6			
NC (12%)			986	2860	218.6
NC (13%)			1099	3420	
AP/HTPB (70/30)					238.5

[a] TMD 100%, BKW EOS, BKWC library Cheetah 2.0.
[b] Blake code in Cheetah 2.0.
[c] Blake code in Cheetah 2.0.

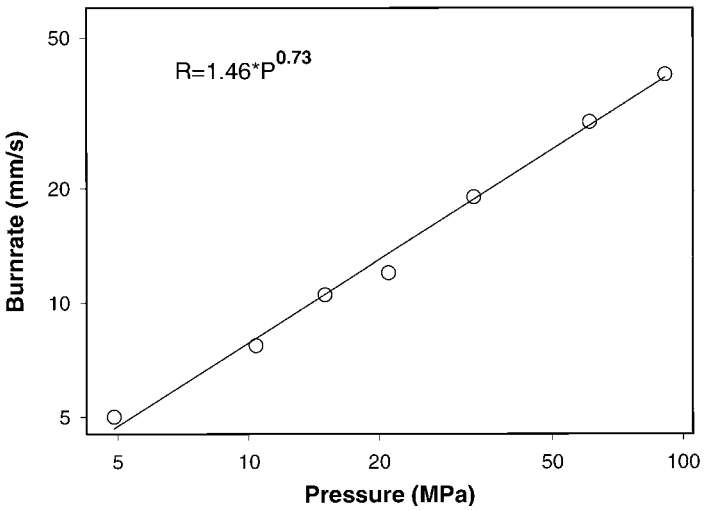

Fig. 8. Burn rate vs. pressure for FOX-12.

8. Discussion and conclusion

Some preliminary conclusions can be drawn from this initial study:

- FOX-12 is less sensitive than both RDX and ADN.
- The thermal stability of FOX-12 is comparable to RDX and superior to that of ADN.
- FOX-12 is a new organic dinitramide salt that is a very promising propellant.
- FOX-12 is a strong candidate as a very low sensitivity propellant ingredient.
- FOX-12 could be used as an ingredient in IM-composition for HE applications.

The results in this paper clearly indicate that FOX-12 is a very promising candidate for a new energetic material, but that several important questions remain to be answered.

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