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SAND2015-3403
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Printed September 2014

Thermal Decomposition of IMX-104: Ingredient Interactions Govern Thermal Insensitivity

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Abstract

This report summarizes initial studies into the chemical basis of the thermal insensitivity of INMX-104. The work follows upon similar efforts investigating this behavior for another DNAN-based insensitive explosive, IMX-101. The experiments described demonstrate a clear similarity between the ingredient interactions that were shown to lead to the thermal insensitivity observed in IMX-101 and those that are active in IMX-104 at elevated temperatures. Specifically, the onset of decomposition of RDX is shifted to a lower temperature based on the interaction of the RDX with liquid DNAN. This early onset of decomposition dissipates some stored energy that is then unavailable for a delayed, more violent release.

ACKNOWLEDGMENTS

All work was conducted under the U.S. DOE/DoD Joint Munitions Program MOU, TCG-III (Energetic Materials). We would like to thank Picatinny Arsenal and Philip Samuels for incorporating us into this program and supplying the formulations and ingredients investigated. Timely discussions with Phil and others at the Army helped in defining the experiments and modifying the program as changes occurred within the Army's IMX-104 qualification program. Denielle Wiese-Smith and Aaron Highley conducted the STMBMS and FTICR experiments and provided initial analysis of the raw data.

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NOMENCLATURE

DOE	Department Of Energy
SNL	Sandia National Laboratories
STMBMS	Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry
FTICR	Fourier Transform Ion Cyclotron Resonance
IM	Insensitive Munitions
DNAN	Dinitroanisole; 1-methoxy-2,4-dinitrobenzene
NQ	Nitroguanidine; 2-nitroguanidine
NTO	Nitrotriazolone; 1,2-dihydro-5-nitro-1,2,4-triazol-3-one
RDX	1,3,5-Trinitrohexahydro-s-triazine
ONDTA	l-nitroso-3,5-dinitrohexahydro-s-triazine

1. INTRODUCTION

1.1. Motivation and Approach

A recent study by this group explored the chemical basis for the thermal insensitivity shown by IMX-101[1]. The study established a shift in the onset of early decomposition steps to lower temperatures, and postulated a dissipation effect induced by this lowered threshold. A study was undertaken to see if similar chemistry was at play in IMX-104. Initial results suggest similar behavior between the two DNAN-based melt-castable mixtures.

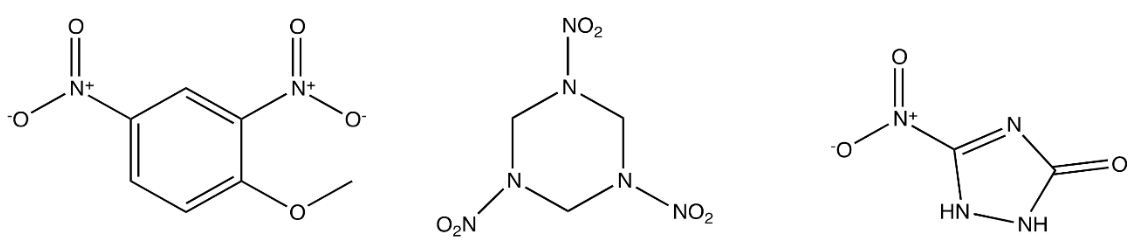
1.2 Technical Background: IMX-104 Ingredients

IMX-104 is a mixture comprised of the ingredients listed in Table 1.

Abbreviation	Common name	Chemical name
DNAN	Dinitroanisole	1-methoxy-2,4-dinitrobenzene
RDX		1,3,5-Trinitrohexahydro-s-triazine
NTO	Nitrotriazolone	1,2-dihydro-5-nitro-1,2,4-triazol-3-one

Table 1. List of IMX-104 ingredients.

The structures of these compounds are shown in Figure 1, below.



1-methoxy-2,4-dinitrobenzene (DNAN) 2,4,6-hexahydro-1,3,5-s-triazine (RDX) 1,2-dihydro-5-nitro-1,2,4-triazol-3-one (NTO)

Figure 1. Molecular structures of the three ingredients in IMX-104: DNAN, RDX, and NTO.

The DNAN serves the primary function to make the material melt-castable, as it has a relatively low melting point.

2. EXPERIMENTAL OVERVIEW

2.1. STMBMS Instrument

Our experiment approach with the Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS) instrument is well-described, both in the aforementioned IMX-101 study [1] and in detail for instrumentation [2]. As shown in the schematic of Fig. 2, heating of the sample in the reaction cell causes evolution of gas-phase products, which form a molecular beam. The molecular beam is directed to a quadrupole mass spectrometer. The mass of the sample is simultaneously recorded on a microbalance, which allows absolute determination of gas evolution rates for each species.

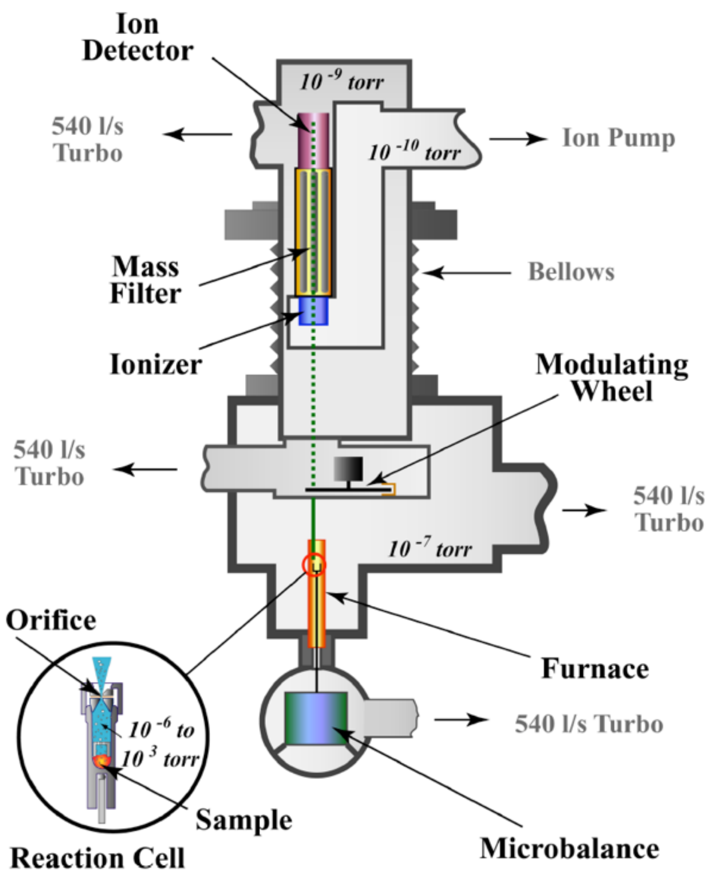


Figure 2. Schematic diagram of the Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS) instrument.

A series of decomposition experiments with thermal ramp temperature profiles are performed on each ingredient as well as a mixture of the three compounds, in order to determine the products formed and the corresponding temperatures at which reactions occur.

3. RESULTS AND DISCUSSION

3.1. Single-Ingredient Behavior

3.1.1. DNAN

The temperature dependence of the sublimation/vaporization from DNAN, as well as thermal decomposition processes, is shown in Figure 3. The species is quite stable; the dominant signal is from sublimation/vaporization of the sample and decomposition is only observed above 200°C.

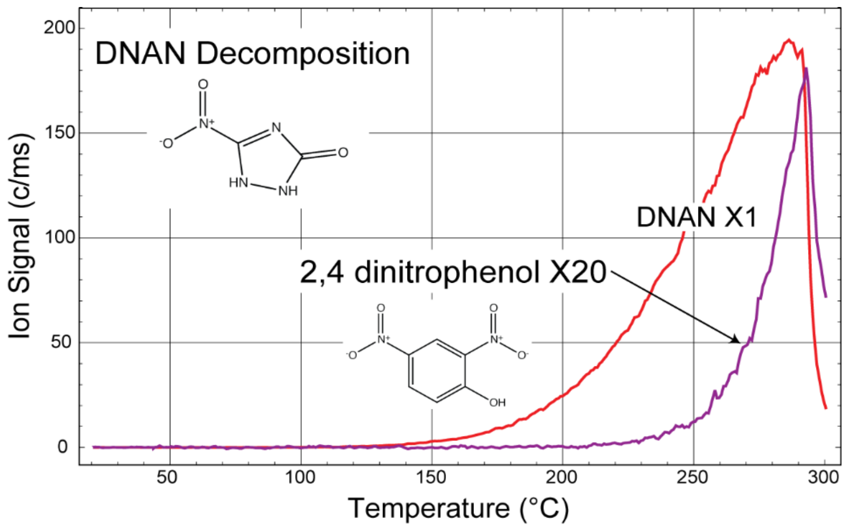


Figure 3. DNAN vaporization and thermal decomposition.

The DNAN decomposition process can be written as:

– DNAN(s) => DNAN(l) => DNAN(g)
– DNAN(l) => 2,4-dinitrophenol + $C_nH_nN_nO_n$.

The behavior is described by low-temperature melting (~94°C) without decomposition, evaporation over broad temperature range, and only at high temperature (>200°C) are gas-phase thermal decomposition products observed.

3.1.2. NTO

The temperature dependence of the sublimation/vaporization from NTO, as well as thermal decomposition processes, is shown in Figure 4. The species shows significant vaporization/sublimation prior to decomposition.

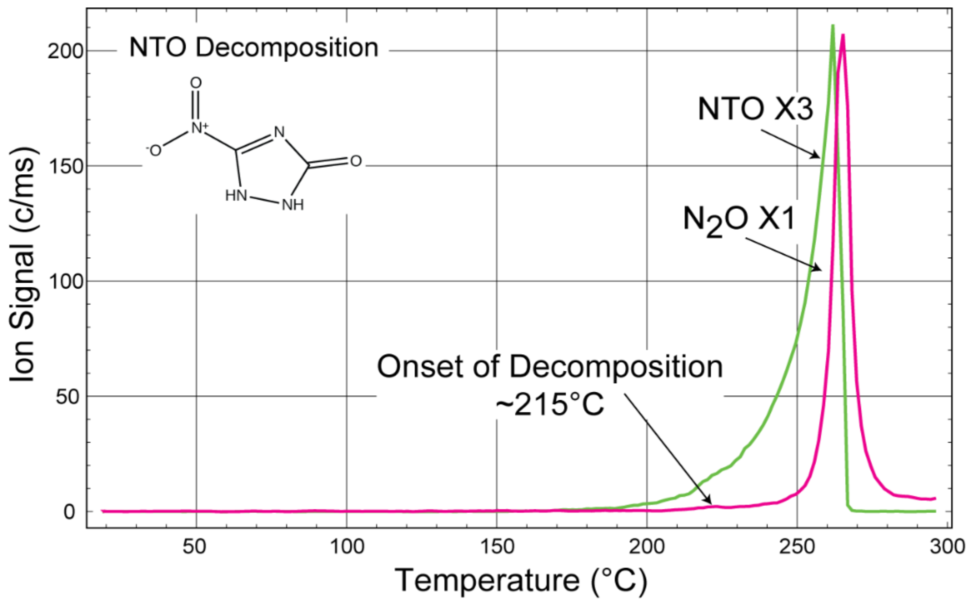


Figure 4. NTO sublimation and thermal decomposition.

The NTO decomposition process can be written as:

– NTO(s) => NTO(g)
– NTO(s) => NTO[-NO](s) + NO(g)
– NTO[-NO](s) => HCNO(g) + CO(g) + N_2(g) + NH_3(g) + NTO[poly].

Thermal decomposition reactions are observed at temperatures of ~215°C and above. The reactions involve nitro-nitrite rearrangement with subsequent bond-cleavage, ring-cleavage reactions, ring-opening and subsequent bond-scissioning reactions, and polymeric residue formation.

3.1.3. RDX

The temperature dependence of the sublimation/vaporization from RDX, as well as thermal decomposition processes, is shown in Figure 5. This decomposition is well studied, and the basic behavior is clear in the figure; RDX shows a low vapor pressure and decomposition at high temperatures.

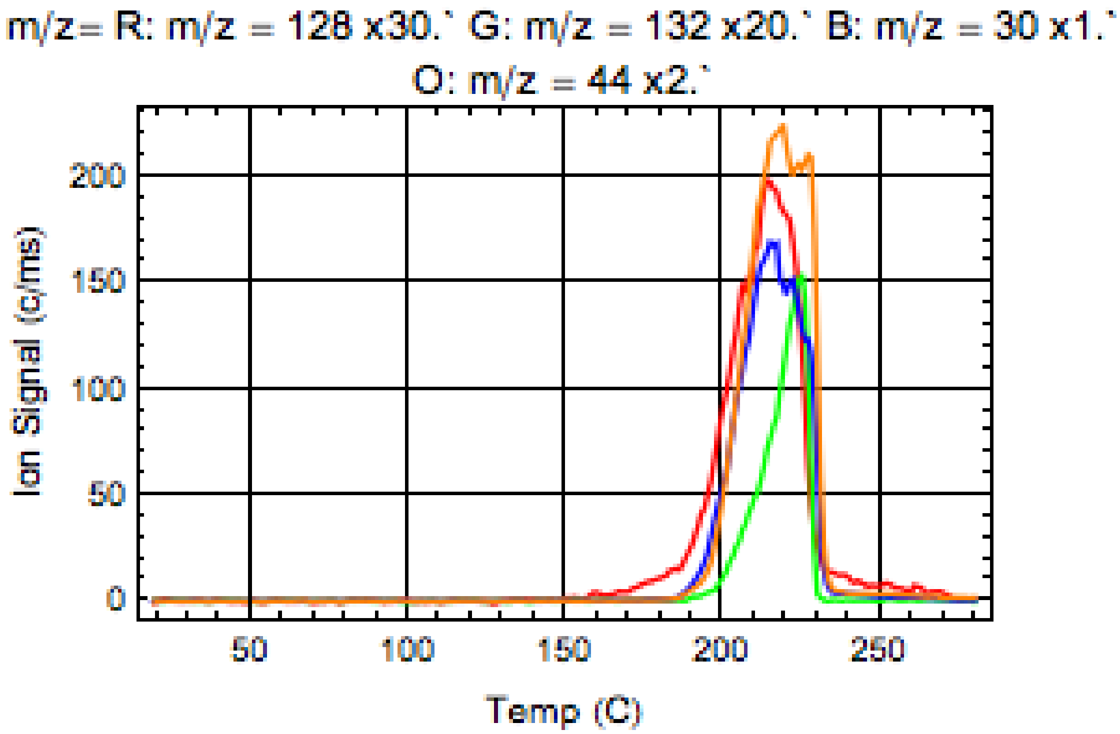


Figure 5. RDX sublimation and thermal decomposition. The red trace represents the RDX parent from sublimation, the green trace is the ONDTA reaction product, the blue trace is the NO reaction product, and the orange trace is the N_2O reaction product.

Although thermal decomposition occurs in the solid phase, it is relatively slow, and rapid thermal decomposition of RDX begins at the melting point of approximately 195 °C for pure RDX. The RDX decomposition process can be summarized as:

– RDX(s) => RDX(g) => s-Triazine + 3HONO => H_2O + NO + NO_2
– RDX(s) => N_2O(g) + HCN(l,g) + CH_2O(l,g) + N_2(g)
– RDX(g) => ONDNTA(g) + NO(g)
– RDX(s) + ONDNTA(g) => RDX*ONDNTA(sur) + NVR(l,s).

In general, RDX decomposition is described by low-temperature sublimation and thermal decomposition upon liquefaction, forming ONDNTA, a variety of gas phase products (N_2O, CH_2O, HCN, N_2, and others) as well as a polymeric nonvolatile residue (NVR).

3.2. Mixed Ingredient Behavior

3.2.1. DNAN with RDX and NTO mixture.

The results of an STMBMS thermal decomposition experiment with a mixture of DNAN and RDX to approximately match IMX-104 proportions is shown in Fig. 6.

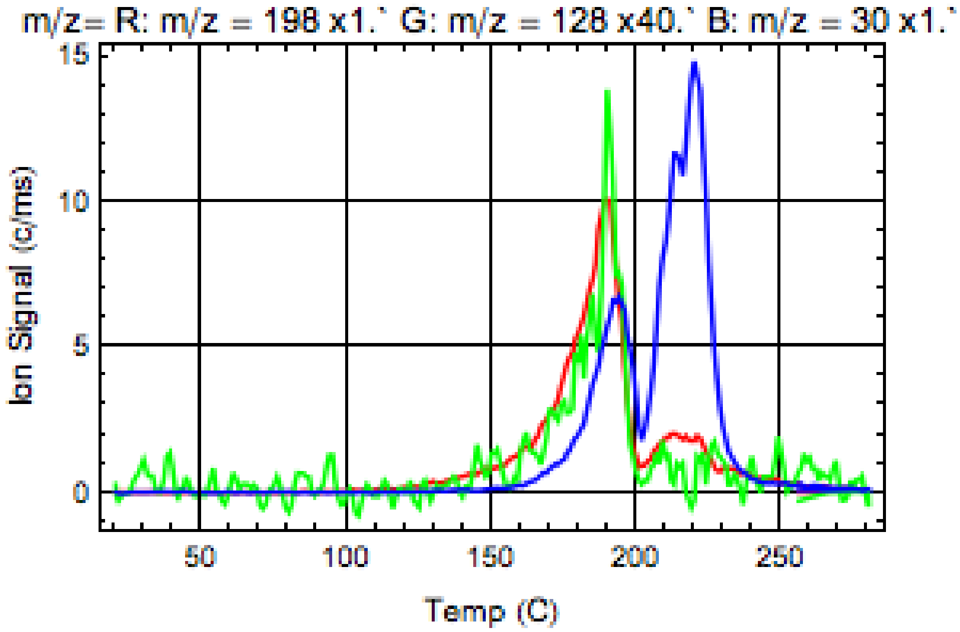


Figure 6. RDX, NTO, DNAN mixture: sublimation and thermal decomposition. The red trace represents the DNAN parent, the green trace represents the RDX parent, and the blue trace represents the NO reaction product from thermal decomposition.

The mixture of the ingredients makes a profound change in the decomposition behavior of the materials. The onset of decomposition for the DNAN shows a low-temperature shift of ~40°C, occurring right after melting in IMX-104. In addition, the onset of NTO decomposition also shows a substantial low-temperature shift of up to 20 – 25°C. Finally, the RDX decomposition shows a shift in onset temperature of more than 10°C, and is complete by 200°C, with very little evolution of gas-phase RDX. In the figure above, the shift of the reaction channel to produce NO product at temperatures well below 200°C, accompanied by a commensurate disappearance of the RDX vapor signal, is clear evidence of the importance of the ingredient interactions promoting low-temperature decomposition.

The implications of these results are that the DNAN lowers the temperature at which the RDX and NTO begin to decompose, and thus begin to dissipate some of the stored chemical energy at a lower temperature than would happen for the pure materials. The RDX decomposition is driven by DNAN interaction lowering the RDX liquid-phase decomposition channel barrier, allowing for an initial release of energy and preventing a delayed and thus more violent response.

4. CONCLUSION

The interaction of DNAN/NQ that is a dominant step in the reactive processes controlling IMX-101 thermal response is paralleled by the DNAN/RDX interaction in IMX-104. IN both cases, the ability of the DNAN to solvate the species at elevated temperatures promotes early onset of reactions that remove stored energy from the system.

5. REFERENCES

1. Sean P. Maharrey, Denielle Wiese-Smith, Aaron M. Highley, Richard Behrens, and Jeffrey J. Kay, *Interactions Between Ingredients in IMX-101: Reactive Chemical Processes Control Insensitive Munitions Properties*, SAND2014-2012. (2012).
2. R. Behrens, Jr., *New simultaneous thermogravimetry and modulated molecular beam mass spectrometry apparatus for quantitative thermal decomposition studies*. Review of Scientific Instruments, v. 58, n. 3, p. 451-461 (1987).

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