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Interactions Between Ingredients in IMX-101: Reactive Chemical Processes Control Insensitive Munitions Properties

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Interactions Between Ingredients in IMX-101: Reactive Chemical Processes Control Insensitive Munitions Properties

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Abstract

Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS) measurements have been conducted on a new Insensitive Munitions (IM) formulation. IMX-101 is the first explosive to be fully IM qualified under new NATO STANAG guidelines for fielded munitions. The formulation uses dinitroanisole (DNAN) as a new melt cast material to replace TNT, and shows excellent IM performance when formulated with other energetic ingredients. The scope of this work is to explain this superior IM performance by investigating the reactive processes occurring in the material when subjected to a well-controlled thermal environment. The dominant reactive processes observed were a series of complex chemical interactions between the three main ingredients (DNAN, NQ, and NTO) that occurs well below the onset of the normal decomposition process of any of the individual ingredients. This process shifts the thermal response of the formulations to a much lower temperature, where the kinetically controlled reaction processes are much slower. This low temperature shift has the effect of allowing the reactions to consume the reactive solids (NQ, NTO) well before the reaction rates increase and reach thermal runaway, resulting in a relatively benign response to the external stimuli. The main findings on the interaction processes are presented.

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NOMENCLATURE

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
TNT	Trinitrotoluene; 2,4,6-trinitrotoluene

1. INTRODUCTION

New NATO STANAG (STANdards AGreement) Regulation 4439 [1] requires all signatories to field fully compliant insensitive munitions. It has been challenging, however, to develop fully IM compliant melt-cast explosive formulations using traditional TNT. This limitation, as well as environmental and toxicity hazard concerns, have required the U.S. DoD, as well as other NATO militaries, to look for alternatives to TNT for use in melt cast formulations that are less sensitive but retain high performance characteristics.

As part of its IM development program, the U.S. Army ARDEC (Picatinny Arsenal) has been investigating the use of DNAN as a melt-castable IM replacement for Comp B (TNT, RDX) in its 155mm artillery shells. DNAN has properties that make it a potentially good melt-cast candidate: its melting point is below 100°C, its liquid-phase vapor pressure is low, its onset of decomposition is well above its melting point, and it has TNT-like density and power. DNAN has also shown good compatibility with many energetic solids in use today. As part of this replacement program, the Army identified IMX-101 (Figure 1) as a good candidate for the 155mm artillery shell Comp B replacement fill. The formulation was the first to be fully IM compliant, passing all 6 of the requisite NATO IM qualification tests (see Figure 2.)

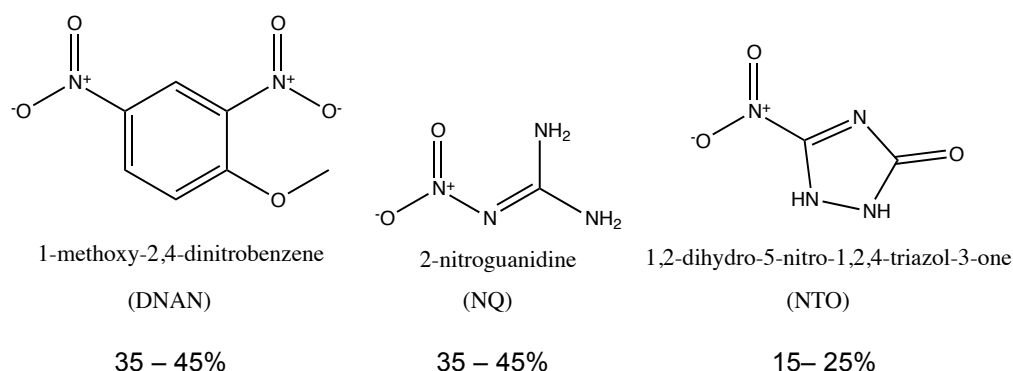


Figure 1. Molecular structures and nominal composition of the three ingredients in IMX-101: DNAN, NQ, and NTO.

The reason for IMX-101's reduced thermal sensitivity was not understood, and our group was approached to investigate this issue.

A general assessment of the possible causes for IMX-101's reduced sensitivity lead to several factors as potential causalities. These factors are listed below.

	Threat	Passing Criteria	Comments
FCO 	Liquid Fuel Fire	Burning	HC Relation : Required for hazard classification Stimulus : Rapid heating response Comments
SCO 	Slow Heating 3.3 °C/Hr	Burning	HC Relation : Required for reduced hazard class Stimulus : Slow heating response Comments : Additional technical studies appropriate
BI 	.50 Cal M2AP 3 round burst	Burning	HC Relation : Required for reduced hazard class Stimulus : Low level kinetic impact Comments : Relevant small arms threat More severe threats exist Additional studies appropriate
FI 	18.6 gram fragment 8300 +/- 300 fps	Burning	HC Relation : Not required Stimulus : Combine shock, mechanical, thermal Comments : Artillery fragments slower Some KE and EFP threats more severe
SD 	Detonation of a single donor	Explosion	HC Relation : Required for hazard classification Stimulus : Output of a like munition Comments : Does not address mixed storage Does not address multiple donor
SCJ 	81-mm Precision shaped charge	Explosion	HC Relation : Not required Stimulus : Shock Comments : More severe threats exist Pragmatic threat considering technology potential

Figure 2. NATO STAGNAG 4439 IM test protocol. Passing criteria for each of the six tests are shown in the table.

HYPTOTHESES:

1. Insensitivity may be an inherent reactive property of the DNAN material. As both NQ and NTO have no implied individual IM property, the DNAN material itself could mitigate the external stimuli for the whole formulation. One potential candidate for this process would be the solid-state phase change in DNAN, leading from the lower melting point polymorph to the higher melting point polymorph, introducing a new reactive pathway by which energy can be dissipated in a benign and controlled fashion.
2. Insensitivity may be an outcome of the melt-cast formulation process during production of IMX-101. During melt casting, new reactive processes could take place that create either new materials in the casting, or that alter normal reactive processes in the existing ingredients to achieve more benign responses to external stimuli.
3. Insensitivity may be due to synthetic impurities or environmental contaminants. Minor species in the material that are produced during synthesis of the main ingredients or are introduced to the formulation during the manufacturing process could alter reaction processes to produce more benign pathways.
4. Insensitivity may be a result of formulation heterogeneity: solids loading and/or particle morphology. Spatial distribution of NQ and NTO could affect reactive transport of

energy/mass in the formulation or the overall effect of particle morphology could also alter the mass/energy transport processes leading to more rapid mixing of material and less localized (violent) responses.

5. Insensitivity may be due to chemical interaction between the main ingredients. The three main ingredients possess their own unique reactive processes when driven by external events that may lead to potentially violent responses, while chemical interactions between ingredients in the formulation may form new, less sensitive compounds or alter existing reactive pathways in such a way as to create a less violent response.

Determination of the dominant causality listed above requires the ability to isolate individual material responses with appropriate design of experiments and corresponding analysis.

The first objective is to develop a reaction process network for each of the individual ingredients. These networks will describe the reactive pathways available in each ingredient as a function of time (temperature), heating rate, partial pressure of gaseous products, sample size and sample phase (condensed or gas). For ingredients where multiple lots are available, each lot will be individually assessed to determine if minor contaminants or impurities in each lot contribute to an overall change in the ingredients reaction network. If changes are observed, additional experiments will need to be conducted to determine which species produce changes and in what compositional quantities changes occur. Additionally, lot variations due to different manufacturers, different synthetic processes, changes in purities of starting material, or different starting material altogether, must be addressed. Manufacturing variations and corresponding stability concerns for IMX-101 do exist and will be addressed here.

Next, one must know how the individual ingredients will react in combination. This is best addressed by starting with binary combinations of ingredients, to determine if any instability or aging processes may occur from certain combinations of ingredient. Additionally, assessment of any overall changes in individual reaction networks will allow us to determine the main cause of any interaction and the conditions under which the interactions occur. These samples are not available as ready-made compounds, and will be made by simple mechanical mixing of each ingredient pair at the time of conducting the experiment.

Finally, the complete IMX-101 formulation will be examined. What one is looking for here is whether new pathways or species are observed that are not a product of the individual ingredients or the binary combinations of each. The assessment must be made as to whether any observed changes are due to the manufacturing process of IMX-101, the interaction of the three ingredients in combination, or from reactions of minor species from different lots of ingredients. Three different IMX-101 lots were available at the time of this study; these included a lot variation where different DNAN material was used, as well as a formulation with a different lot of NQ. No formulations with NTO variations were available. The melt-cast formulation process was not altered in the available lots, and this assessment was not possible for this study.

The approach we undertook to investigate this set of hypotheses is stated below.

APPROACH:

1. Measure the mass spectrum of each material used in the formulation. Identify the parent compounds and any impurities/contaminants. Compare for different lots, or modifications of each material. What species are present, when do they evolve, and how much evolves?
2. Determine the onset of thermal decomposition and decomposition chemistry for each material, and for each lot. What is the decomposition process? What conditions control the process? What affects do minor species play in the decomposition?
3. Examine the thermal stability and decomposition behavior of binary combinations of DNAN, NQ, and NTO. Does any combination of ingredients form an unstable reactive pair? What pairs interact? How do they interact? Is solubility important? What conditions control the interaction?
4. Examine decomposition behavior of three-component DNAN/NQ/NTD mixtures. Does phase of mixing of the ingredients or rate of mixing control the interaction? Which ingredient controls the mixing? Do all three materials participate in the interaction?
5. Compare thermal stability of and reaction processes observed during decomposition of (i) each of the main ingredients, (ii) binary combinations of the main ingredients, and (iii) all three ingredients together, to evaluate the overall effect of multi-component interactions. What are the dominant processes controlling IMX-101 thermal decomposition?
6. Determine whether lot variations (synthetic route, particle morphology, purity) affect the decomposition processes. Are the main ingredients responsible, or are minor species the driver?

Three experimental configurations are used for the approach outlined above:

1. Mass spectrometry experiments using large samples (to prolong experiment time) with large orifices and slow heating rates. These experiments will tell us what is present in each ingredient, binary pair, and IMX-101 formulation. Additionally, we will observe when each species evolves (onset, peak, and depletion), and the quantity of minor species present in each lot, if any. Finally, this set of experiments will show us the electron-bombardment ion-fragmentation pattern for each ingredient and allow us to track each species by its dominant ion mass as well as eliminate overlap of species signals at the same mass-values.
2. Decomposition experiments using smaller orifices and more complex heating profiles, along with sample size variations. These experiments will address the main features of the reaction networks for the ingredients, binary pairs, and formulation. Additionally, the extent of condensed-phase versus gas-phase decomposition, phase change (melting), secondary gas/condensed-phase interactions, solubility, and surface reactions can be addressed with these sets of experiments.
3. Flow reactor experiments allow us to separate individual ingredients within the reaction cell to look at effects of gas-phase transport, diffusion, and solubility conditions on any observed interaction.

This report presents the interim results for the approach listed above.

2. EXPERIMENT

Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS) [2] – [4] was used to investigate the thermal decomposition chemistry of the IMX-101 ingredients and mixtures at small scales. Data acquired with the STMBMS apparatus are used to develop reaction networks that describe the detailed chemical and morphological processes that occur at elevated temperatures. For this study, the technique was used to investigate the decomposition behavior of the individual ingredients and the potential for chemical interactions between the main ingredients of the IMX-101 formulation.

An overview [5] describes the experimental methods and numerical algorithms used to examine and characterize the reactions of energetic materials at elevated temperatures. The experimental methods utilize: (1) the STMBMS instrument and associated numerical data analysis algorithms to measure vapor pressures and investigate the thermal decomposition processes of compounds and mixtures, and (2) a Fourier Transform ion cyclotron resonance (FTICR) mass spectrometer to aid in identifying molecular fragments and decomposition products.

2.1. Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS)

Details of the STMBMS instrument and analysis methods have been described previously [5]-[7]. The basic features of a thermal decomposition experiment using the STMBMS instrument are illustrated in Figure 3. A small sample of energetic material (2-10 mg) is placed in an alumina reaction cell (free volume of 0.227 cm³), which is sealed with a cap assembly containing either a disk of 25 μm thick gold foil with a small pinhole (2.5-50 μm) at its center or a ceramic cup with a 30-1000 μm orifice at its center. The reaction cell is heated in a controlled manner using a thermocouple and programmable thermal controller to measure and control the temperature of the cell. As the reaction cell is heated, volatile compounds are generated due to sublimation/evaporation and thermal decomposition of the sample. These vapors fill the free volume of the reaction cell, causing it to pressurize. The pressurized vapor flows through the orifice and expands into vacuum, forming a molecular beam. The resulting molecular beam is directed into a quadrupole mass spectrometer, where the relative abundance of each constituent is measured. The reaction cell also sits atop a microbalance, which records the change in mass of the sample as it is heated and undergoes sublimation/evaporation and decomposition. Together these measurements allow determination of the time-and-temperature-dependent rate of formation of each gaseous species that evolves from the heated sample. The measurements also provide the vapor pressure of gaseous species that are in quasi-equilibrium with material in condensed phases.

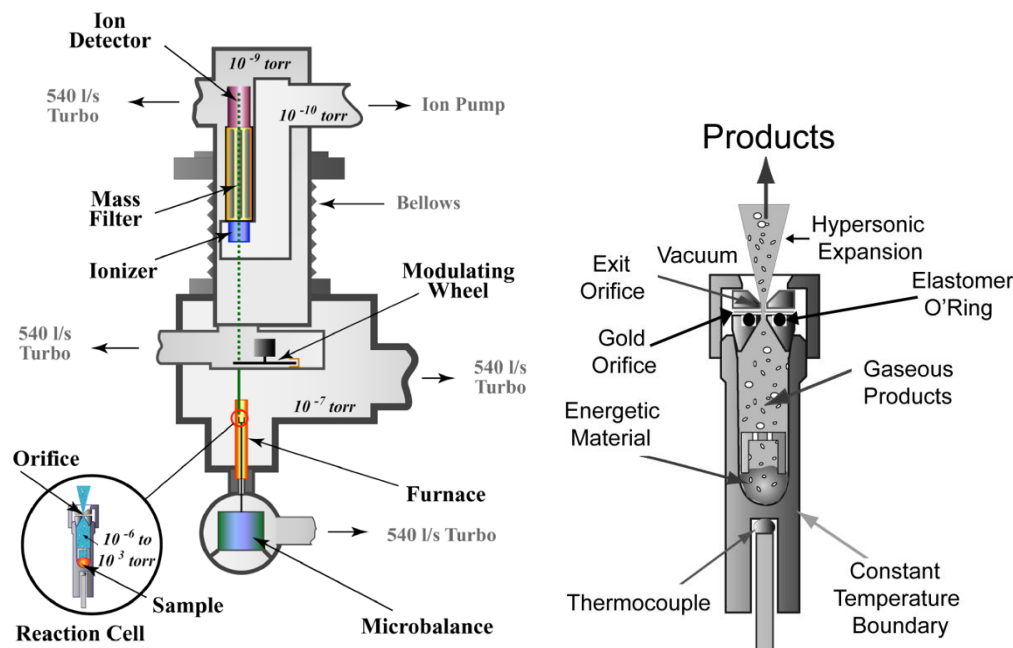


Figure 3. (a) Schematic diagram of the Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS) instrument. Heating of the sample in the reaction cell causes evolution of gas-phase products, which form a molecular beam. The molecular beam is directed to a mass spectrometer, where species are ionized and detected using 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. (b) Schematic diagram of the reaction cell illustrating a typical sample configuration used in an STMBMS experiment.

The pressure of gases within the reaction cell is determined by the diameter of the orifice and the experimental conditions. The gas pressure within the cell is determined by a steady-state balance between the rate of gas formation from the sample and the rate of exhaust through the orifice. Smaller orifices will produce higher pressures for a given gas formation rate from the sample. For compounds in two-phase quasi-equilibrium, the pressure is determined by the temperature of the reaction cell and the thermal properties of the compounds. In this case, a smaller orifice results in less of the gas exiting the reaction cell.

The data used to characterize the thermal decomposition processes are the identities and rates of formation of the different vapors that flow through the orifice and out of the reaction cell over a range of experimental conditions. The reaction conditions are controlled by altering the sample size, temperature, heating rate, orifice diameter and volume of the reaction cell.

2.2. Fourier Transform Ion Cyclotron Resonance (FTICR) Mass Spectrometry

A Bruker Daltonics APEX-II Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer is used to unambiguously identify compounds that evolve from the samples. It is a high mass resolution ($m/\Delta m > 100,000$) and mass accuracy (< 1 ppm) ion-trap-based mass

spectrometer. The high mass accuracy of this instrument allows unambiguous determination of the empirical formula for each mass-value observed in a mass spectrum. Operation of this instrument under conditions similar to the STMBMS instrument allows chemical analysis results from the FTICR to be matched to the temporally correlated product distribution spectra obtained with the STMBMS instrument.

A basic chemical analysis thermal decomposition experiment using the FTICR mass spectrometer is straightforward. A 1mm ID x 9mm L quartz tube (internal volume: 0.0071 cm³) is loaded with ca. 1 mg of material and the open end of the tube can be either left open or “necked-down” with a methane-oxygen flame to produce an exit aperture as small as 5 μm in diameter. The resulting reaction cell is mounted in the heated tip of a direct insertion probe (DIP) whose temperature is controlled by a programmable temperature controller (Omega model CN3000). The DIP probe is inserted into the FTICR mass spectrometer with the tip of the probe positioned at the entrance of an electron-bombardment ionization (EI) source. Neutral gaseous species exiting the quartz reactor are ionized in the EI source and extracted into the FTICR mass spectrometer for analysis.

3. RESULTS

Multiple lots of the main ingredients and the IMX-101 formulation were used in this study to determine whether the thermal response behavior was an inherent property of the formulation, or due to reactions involving minor impurities or contaminants as the main drivers.

DNAN, as typically manufactured, has a high water content. This material will be referred to throughout this document as “wet” DNAN. When used in melt casting, the melting pots are open-topped kettles, and water evaporates continuously from the melt-phase material. This results in a substantial, although not complete, loss of water from the formulation during melt casting of IMX-101 and results in difficulty assigning the final weight percent composition, as the amount of water lost is not measured. At one point, an additional step was added in the manufacturing process that removed this water by holding molten DNAN in an open-topped continuously-mixed kettle. We observed this “dry” DNAN to have substantially, although not completely, reduced water content. The drying process also eliminated some water-soluble, but currently unidentified, minor impurities from the DNAN. We did not observe any change in the onset of decomposition in dry DNAN as compared to wet DNAN. During manufacture, dry DNAN form showed significantly increased rates of melt-cast failures – specifically formation of cracks and voids while cooling in the munition case – and as a result, dry DNAN has been eliminated from the manufacturing process in favor of wet DNAN. Therefore, aside from the preliminary experiments described above, we used wet DNAN (and IMX-101 produced using wet DNAN) in all of our thermal decomposition experiments and investigations described below.

Two different lots of NQ were analyzed during this investigation. The early lot was of lower purity and contained more irregularly-shaped particles. The later lot had been recrystallized to remove some of the impurities and to improve crystal form – specifically, to produce more regular and more spherical particles. During the course of this investigation, the earlier lot was dropped from consideration for production of IMX-101. Therefore, aside from some preliminary experiments on the earlier lot, we used the later high-purity NQ in all of our investigations below.

Only one lot of NTO was used during the course of this study. Throughout our experimental program, the same lot of NTO has been used and no attempt was made to evaluate any alternative lot of NTO.

Finally, three different IMX-101 lots were available for study. The original form used wet DNAN with unrecrystallized NQ. We were also provided with IMX-101 using dry DNAN and unrecrystallized NQ. The third lot was acquired several months later, after the dry-DNAN-based IMX-101 was eliminated as a viable manufacturing option. This lot uses wet DNAN, and also uses the new recrystallized NQ. Initial studies with all three lots showed no substantial difference in their thermal decomposition behavior.

In summary, no substantial differences involving interactions between the main ingredients and subsequent changes in the thermal decomposition processes for the main ingredients was observed with the various lots of materials supplied. As such, the focus of the study shifted to the

ingredients and formulation used in manufacture and subsequently fielded in the 155mm artillery shell.

Table 1 shows the STMBMS experimental configurations used for the different materials in this study. Column 1 shows the individual material used in each experiment as well as its lot identifier. A brief description of each sample is listed in column 2, while column 3 shows the corresponding experiment type conducted on each material; mass spectrum (MS), vapor pressure (VP), decomposition (Dec), Flow Reactor, or FTICR. Column 4 shows the corresponding sample mass for each experiment type conducted, and the corresponding orifice size is shown in column 5. The thermal profile used in each experiment is shown in column 6, and final sample residue, as indicated by the microbalance, is shown in column 7.

Table 1. Summary of STMBMS experiments on IMX-101 and ingredients.

Material	Description	Experiment Type	Sample (mg)	Orifice (μm)	Heating Profile	Residue (mg)
<u>* DNAN</u>						
K282	Wet	MS	11	500	Ramp	0.25
		VP	12	100	Stepped Isothermal	2.75
		FTICR	< 1	1000	Ramp	Unknown
		Dec	15	10	Ramp	0
		Dec ^a	7 DNAN, 3 Other ^c	10	Ramp	2.2 (NTO), 1.75 (NQ), Unknown (IRDX)
BA06-19	Dry	MS	12	500	Ramp	0
		Dec	15	10	Ramp	0
<u>* NQ</u>						
D405	Low Purity	MS	3	500	Ramp	0.3
		VP	5	100	Stepped Isothermal	2.4
		FICR	< 1	1000	Ramp	Unknown
10NQ8-11	High Purity	MS	3	1000	Ramp	0.6
		Dec	2	25	Ramp	0.6
<u>* NTO</u>						
B305	Used in Manufacture	MS	4	500	Ramp	0
		VP	4	100	Stepped Isothermal	2.5
		FTICR	< 1	1000	Ramp	Unknown
		Dec	3	10	Ramp	0.2
<u>* IMX101</u>						
K375	Wet DNAN	MS	5	1000	Ramp	0.2
		FTICR	< 1	1000	Ramp	Unknown
		Dec	5	30	Ramp	0.8
IMX101-21	Dry DNAN	FTICR	< 1	1000	Ramp	Unknown
		Dec	5	30	Ramp (1) & Isothermal (1)	0.9 (Ramp), 3.4 (Isothermal)
IMX101-34	Wet DNAN/ High Purity NQ	Dec	5	40 (1), 20 (2), 10 (1), 2.5 (1)	Ramp (3), Isothermal (1), Stepped Isothermal (1)	1 - 1.7 (Ramps), Unknown (Isothermal), 1.7 (Stepped Isothermal)
		Dec ^b	4 NQ, 5 NTO	50	Ramp	2.5
		Flow Reactor ^d	5 NT, 5 NQ, 5 DNAN	30	Ramp	4.3
			5 NTO, 2 NQ, 5 DNAN	30	Ramp	1.1
			5 NTO, 5 NQ	30	Ramp	3.1

^a DNAN was mechanically mixed with another ingredient in the bottom of the STMBMS reaction cell

^b NTO and NQ were mechanically mixed in the bottom of the STMBMS reaction cell

^c Other refers to either NTO-B305, NQ-10NQ8-11, or IRDX

^d NQ or NQ/DNAN loaded into bottom of reactor, NTO loaded into top section of flow reactor

Due to the relatively high vapor pressure of DNAN, a larger sample size was used with this material to avoid depletion of the sample before the end of the experiment. The smaller orifice used in the DNAN experiments also helps minimize the exhaust rate from the cell, prolonging

the experiment. A smaller orifice was used for NTO to help confine material to investigate secondary interactions between gas-phase and condensed-phase species. Smaller orifices were chosen for NQ and IMX-101 to allow observation of weaker species during decomposition, without compromising formation of secondary reactions or depleting samples before the reactions were complete.

Table 2 shows a general summary of the STMBMS thermal decomposition experiments on the various IMX-101 ingredients and formulation. The table shows the material investigated, onset of decomposition observed by the first formation of a decomposition product, the overall decomposition range, the temperature at which the peak signal intensity for decomposition occurs, the overall shift in decomposition temperature (for IMX-101 only), and the relative amount of residue remaining (residue mass/sample mass).

Table 2. Summary of thermal decomposition results from STMBMS experiments.

Material	Decomposition Onset (°C)	Decomposition Range (°C)	Peak Decomposition (°C)	Decrease in Onset (°C)	Residue (% Sample)
DNAN	210	210 - 300	260	-	0
NQ	175	175 - 250	240 (Decomposition), 250 (Polymerization)	-	~33
NTO	215	215 - 280	265	-	~7
IMX-101	160 (DNAN), 145 (NQ), 165 (NTO)	160 – 210 (DNAN), 145 – 240 (NQ), 165 – 225 (NTO)	180 (DNAN), 230 (NQ Decomposition), 205 (NTO)	50 (DNAN), 30 (NQ), 50 (NTO)	16 – 34 ^a

^a Depending on experiment conditions

From Table 2, we see that the onset of decomposition for DNAN occurs at 210°C, well above its melting point (~90°C), and decomposition occurs over a very broad range (210-300°C). The high onset temperature makes DNAN an excellent melt cast material, as it can be cast well above its melting point and will not decompose during the melt-casting process. NTO has a slightly higher onset temperature than DNAN (215°C), and decomposes over the 215-280°C range. Finally, NQ decomposition begins well below either of the other ingredients (175°C), but occurs over a fairly broad range (175-250°C). These three IMX-101 ingredients possess a great deal of overlap in their decomposition temperature ranges. This indicates that there may be substantial interactions between the ingredients and their byproducts during thermal decomposition of the IMX-101 formulation.

The degree of interaction between the ingredients during thermal decomposition of IMX-101 is displayed in Column 5 of Table 2. We see that the onset temperature for the decomposition of each ingredient in IMX-101 shifts downward in temperature anywhere from 30°C (NQ) up to 50°C (DNAN and NTO). As thermal decomposition shifts substantially to lower temperatures, it

rates of reaction will be lower, and subsequent thermal response of this formulation is going to be similarly less violent.

Figure 4 shows the ion signals as a function of temperature in the STMBMS experiments conducted on DNAN, NQ, NTO and IMX-101. The upper set of plots show the decomposition of DNAN, NQ, and NTO from left to right, while the lower plot shows decomposition of IMX-101. Shown in each plot is the parent ion signal, which indicates the vaporization of each individual species, as well as a dominant decomposition product for each species, demonstrating the overall temperature range over which each ingredient decomposes.

DNAN evaporation is seen to begin around 130°C, which is approximately 40°C after melting has occurred, indicating that the liquid-phase DNAN has a fairly low vapor pressure while IMX-101 is being formulated (<100°C) and also at the temperature where melt-casting of the 155mm artillery shell fill occurs (~120°C). Approximately 80°C higher, decomposition begins, as indicated by evolution of the 2,4-dinitrophenol decomposition product. This is the only DNAN decomposition product we observe. The peak decomposition temperature occurs approximately 5°C higher than the peak evaporation temperature and both evaporation and decomposition signals are highly correlated during the depletion stage of the decomposition.

The onset of the NQ sublimation and decomposition are seen to occur together at approximately 175°C, and a later condensed-phase polymerization reaction begins around 190°C. The high sublimation temperature indicates that NQ is not evolved to any measurable extent during IMX-101 formulation or melt-casting of the munition fill. The NQ decomposition process is dominated by simple bond-cleavage reactions to release ammonia (NH₃) and N₂O. The polymerization reaction involves condensed-phase fragments from the NQ decomposition linking together to predominantly form a stable melamine product. The decomposition reaction peaks around 225°C and rapidly decelerates, indicating all available NQ has been converted to its condensed-phase fragments. The polymerization reaction peaks approximately 15°C after decomposition has peaked and rapidly decelerates, indicating the depletion of available fragments species for polymerization.

NTO sublimation and decomposition also begin under similar conditions, at approximately 215°C. The NTO continues to sublime throughout the decomposition, while the corresponding decomposition process goes through several subsequent channels resulting in the release of different gas-phase products. Again, the high onset temperature for NTO would indicate a minor vapor pressure for NTO at temperatures corresponding to IMX-101 formulation or melt-cast manufacturing. The decomposition product shown in Figure 4 is N₂O, which is formed during the final stage of the condensed-phase decomposition and marks the end of the decomposition process with formation of a solid residue that remains after the decomposition has completed.

Decomposition of Individual Ingredients

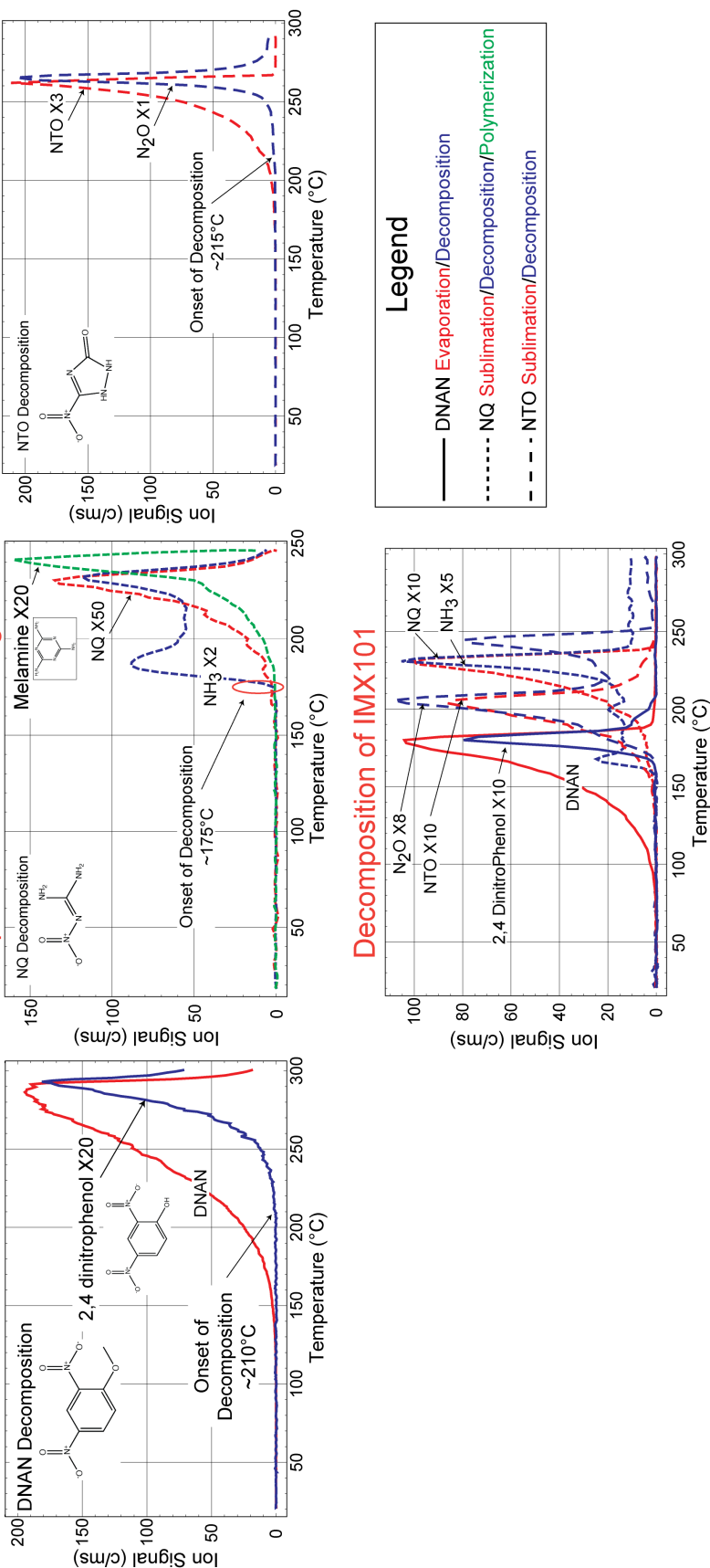


Figure 4. Main ion species from the STMBMS measurements of the thermal decomposition of the individual ingredients and the IMX-101 formulation. Upper plots show the evaporation/sublimation signals and a representative decomposition species for each ingredient. Lower plot shows the evaporation/sublimation signals and representative decomposition products for the IMX-101 formulation. The legend key provides the identifiers for each ingredient and decomposition species used in the plots.

IMX-101 decomposition, shown in the lower panel of Figure 4, shows significantly decreased onset temperatures for all ingredients, both for sublimation/evaporation and thermal decomposition. DNAN and NTO decomposition shows a shift to lower temperature of about 50°C, while the NQ onset shifts lower by approximately 30°C. Notably, the NTO sublimation/decomposition occurs slightly higher in temperature than NQ, while in IMX-101, NTO sublimates/decomposes after NQ decomposition, but well before NQ polymerization. These results indicate a significant interaction between the three ingredients has occurred that has shifted the normal decomposition process for each ingredient to substantially lower temperatures.

The results from the binary ingredient experiments did not show any significant changes in the decomposition pathways for any of the ingredients combinations and were not included in Figure 4. It is possible that by simply mechanically mixing these binary mixtures, we did not achieve the intimate contact that would have occurred if we had used melt-formulated binary mixtures.

Figure 5 shows optical micrographs of DNAN, NQ, NTO and IMX-101 samples both before and after decomposition. The upper set of plots shows optical images for DNAN, NQ and NTO from left to right, while the lower plot shows images for IMX-101. The “pristine” marker indicates samples loaded into a reaction cell prior to decomposition, while “residue” indicates the material remaining in a reaction cell after complete decomposition.

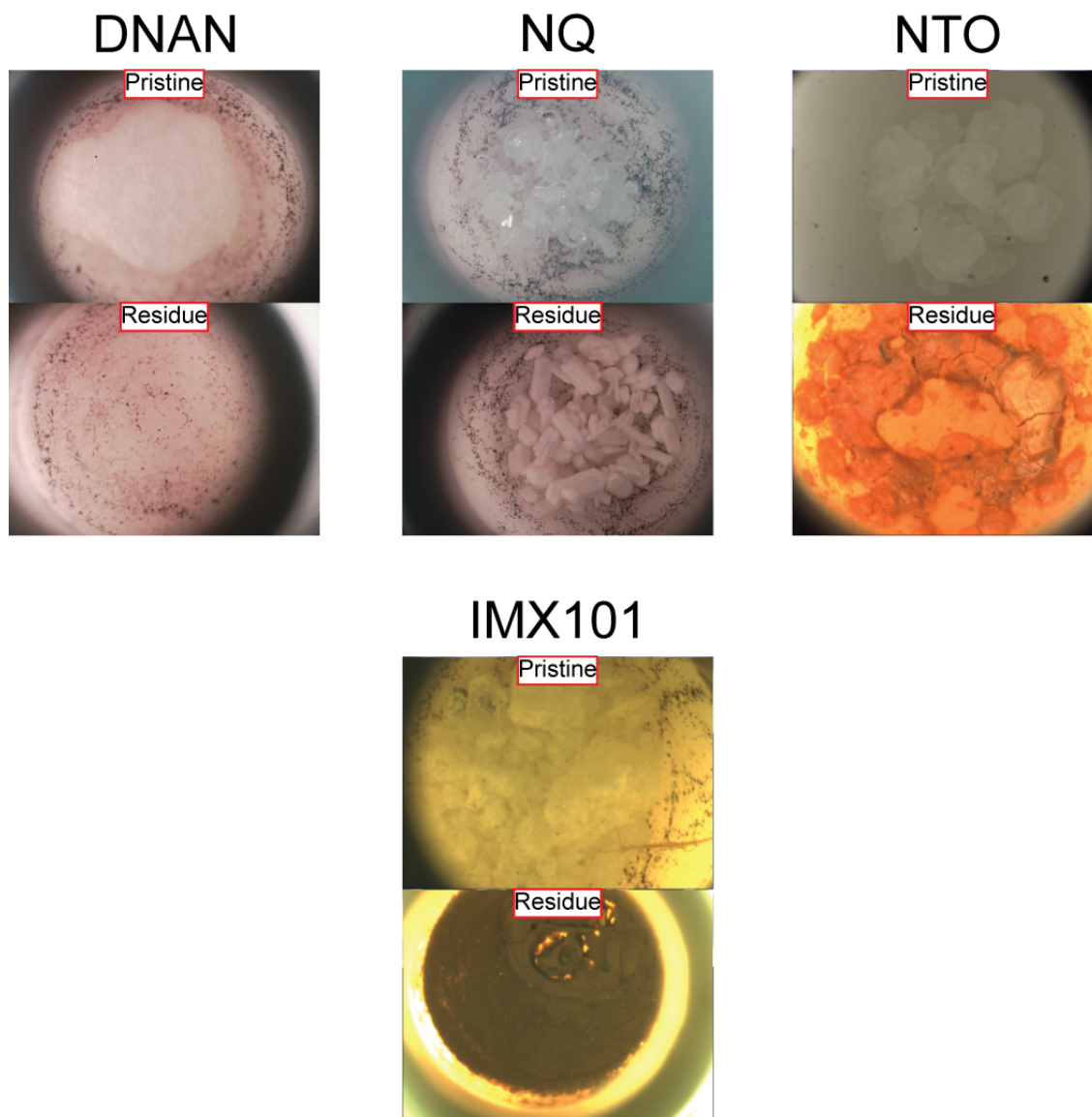


Figure 5. Optical micrographs showing the samples as loaded in the reaction cell before and after each STMBMS experiment. Upper photos show the individual ingredients before and after decomposition, lower photos show the IMX-101 formulation before and after decomposition. “Pristine” denotes samples before decomposition, and “Residue” denotes samples after decomposition is complete.

The pristine DNAN material can be seen as a smooth, uniform, relatively homogeneous sample after loading into the reaction cell. After fully decomposing, no apparent residue material remains in the reaction cell, and DNAN is seen to fully deplete during decomposition.

Pristine NQ is seen as a rather inhomogeneous pile of large, elongated, pointed particles with a smooth surface appearance. Particles are relatively translucent in appearance under normal light. After decomposition has completed, the recovered NQ sample shows similar morphological features as the pristine material, but is now opaque in appearance, and possesses a white, grainy surface roughness. All sharp points or edges observed with the pristine material have been

substantially rounded. In general, particles have gone from translucent, regular, with sharp features and a smooth surface to opaque white, regular, with smooth features and a rough surface.

Pristine NTO has the largest particle sizes of the three ingredients, and appears as relatively uniform, regular translucent particles, with smooth features and surfaces. The decomposed NTO sample displays morphological features similar to the pristine sample, but shows a significant reddish-orange color change on the surfaces as well as general roughening of the surface and possible particle size increases.

IMX-101 does not behave like any of the three individual ingredients. The lower plot in Figure 5 shows pristine and decomposed IMX-101. The pristine material appears as a mixture of the three ingredients, with readily apparent NQ and NTO particles and an opaque white coating of DNAN. The residue material, however, is quite unlike the residues of the decomposed individual ingredients. We observe a homogeneous thin film that is a dark flat brown in color. The significant difference in appearance of the IMX-101 residue indicates a strong interaction between the three ingredients. The uniform color and coverage of the residue indicate that liquid-phase DNAN played a dominant role in controlling this interaction process.

Figure 6 shows a select set of optical images from a hot-stage optical microscopy experiment conducted on IMX-101. The hot-stage experiment used a 1°C/minute heating rate, with temperature ranging from 25 to 300°C, and a sample mass of less than 1 mg of IMX-101. The pyrex glass reactor had an orifice of approximately 30 μm in diameter formed using a methane/oxygen micro-torch. Magnification for this experiment was 30X, and 1730 optical images were acquired at 11-second intervals to cover the complete temperature range. The set of images in Figure 6 show the main features observed and the temperature at which they occurred. The following describes what is shown in the images:

1. **94 to 98°C:** DNAN melts and evaporates from the reactor tube in this temperature region. Above 98°C, the reaction tube contains individual NQ and NTO particles, with a surface coverage of melt-phase DNAN on their surfaces.
2. **175°C:** The individual NQ and NTO particles decompose, with the color change indicating interaction between NQ and NTO on the surfaces of the particles.
3. **182.5°C:** A liquid-phase homogeneous residue begins to form. All NQ and NTO particles have been fully consumed.
4. **188°C:** The residue has continued to decompose. Polymerization of the small chain fragments from complete NQ/NTD decomposition has started.
5. **234°C:** The final, solid polymer residue has fully formed. Continued decomposition of this residue is not observed. All remaining optical images covering 234 to 300°C show no changes in the residue observed at the temperature of this image.

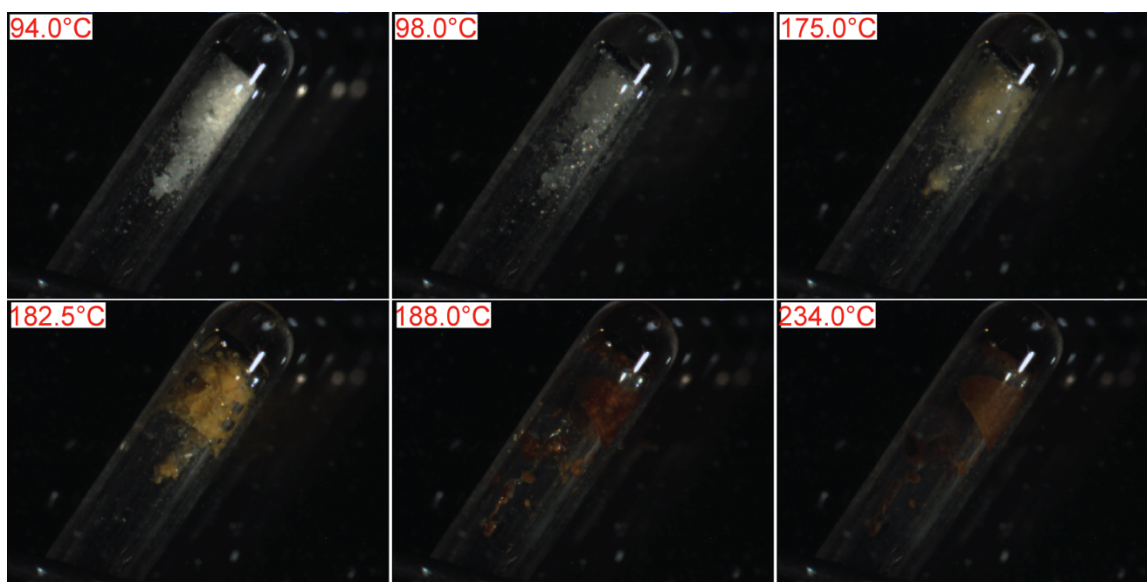


Figure 6. Optical micrographs extracted from a hot-stage thermal decomposition of IMX-101. Images show the main sequence of morphological events occurring during the complex decomposition process. Approximate temperature is included on each image to illustrate how the state of the material changes with temperature/time. Specific color changes are an indicator of the high degree of heterogeneity in the overall decomposition process, and mark the location of specific localized reaction environments.

The hot-stage images correlate with the mass spectrum signals observed in the IMX-101 STMBMS experiments (Figure 4) and the optical images of the pristine and decomposed samples (Figure 5). The color metric and morphological changes observed clearly shows that the IMX-101 decomposition is much more complex than the decomposition of any of the ingredients. The low magnification in the hot-stage experiments make it difficult to see spatial distribution of color or morphological (phase) changes, but provides enough detail to see that the interactions of the ingredients during decomposition follows a sequential set of reactions, including phase changes (solid/liquid). It is also apparent from the images that while gas phase species are evolved, the dominant interactions are condensed phase processes.

The above results provide the information necessary to create a generalized set of reaction processes for the ingredients and the IMX-101 formulation. The next section will discuss the development of these reaction processes and present a general theory we have developed for the reactive processes describing how the chemical interactions alter the thermal response and possibly contribute to the thermal IM properties of IMX-101.

4. DISCUSSION

The STMBMS results were used to develop a basic thermal decomposition reaction mechanism for DNAN, NQ, NTO, and IMX-101. The DNAN results shown in Figure 4, and discussed above, indicate a simple decomposition process, which is summarized in Figure 7. The only observed species are DNAN and the 2,4-dinitrophenol decomposition product. DNAN has a melting point of approximately 90°C, and melting is the first step in the decomposition process. DNAN vapor is observed well after the sample has melted, and indicates that solid-phase DNAN has a minimal vapor pressure. From this, the first reaction step is the melting of DNAN (D1), followed by the equilibrium evaporation of liquid-phase DNAN (D2). The evolution of gas-phase 2,4-dinitrophenol does not track with the evolution of gas-phase DNAN, indicating that it is a condensed-phase product. The decomposition process that forms 2,4-dinitrophenol from DNAN is a simple bond-rearrangement reaction involving a hydrogen transfer from the methyl subgroup to the oxygen atom on the methoxy group and subsequent release of CH₂. The sudden, sharp onset of the evolution of 2,4-dinitrophenol indicates that it is not a simple vapor equilibrium release, but a form of condensed-phase phase separation. A DNAN/2,4-dinitrophenol eutectic formation (D3) and subsequent equilibrium balance between gas-phase DNAN and 2,4-dinitrophenol and liquid-phase eutectic is consistent with this result (D4). The lack of any residue from the decomposition of DNAN is consistent with this mechanism.

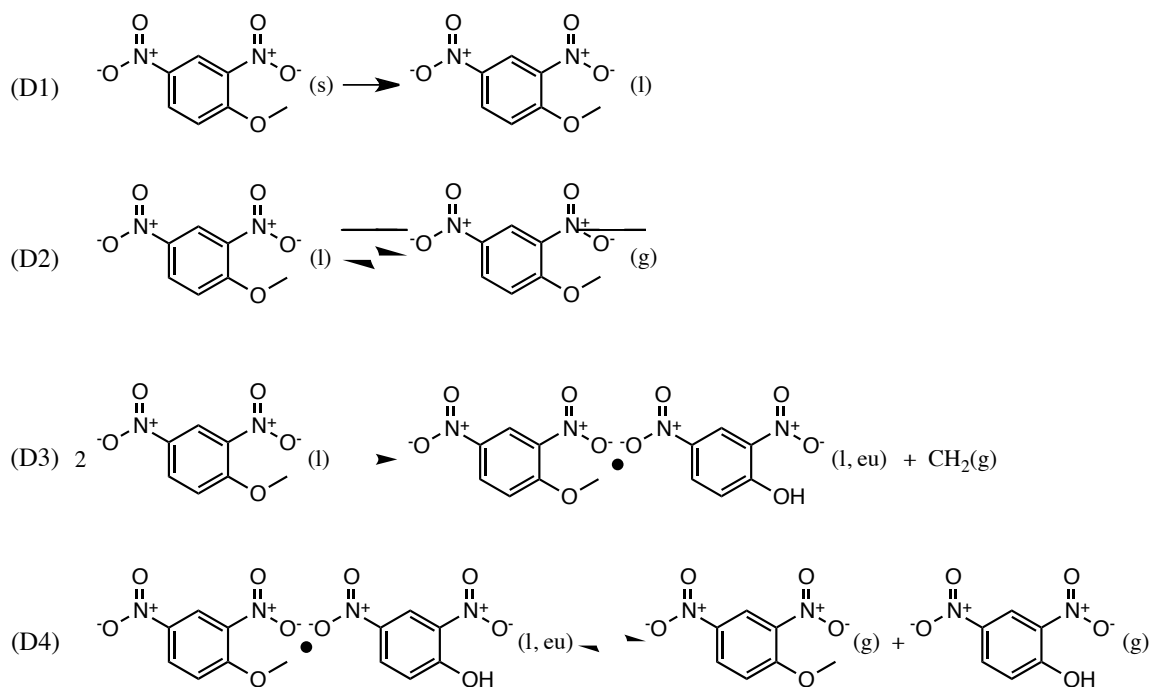


Figure 7. DNAN thermal decomposition mechanism.

The NQ decomposition process (Figure 8) is more complex. The observation that the residue has preserved the basic initial shape of the starting material indicates that this decomposition process does not go through a liquid-phase state, and all reactions occur in the solid phase. In Figure 4, the first step is a parallel competition between equilibrium sublimation of NQ (NQ1) and a

direct, bond-scissioning reaction of NQ to form NH_3 combined with a bond-rearrangement reaction to form N_2O (NQ2) and an as-yet unidentified reactive fragment. The reactive fragments from the decomposition reaction combine to form a stable melamine product (NQ3). The melamine product undergoes two subsequent competing reactions, an equilibrium sublimation (NQ4), and further reaction with the NQ fragment from the decomposition reaction to form the final residue (NQ5). The shape and opaque nature of the final residue is consistent with a polymeric type material, while the fact that the residue is approximately 1/3 of the starting material would indicate a small chain, densely packed polymeric residue.

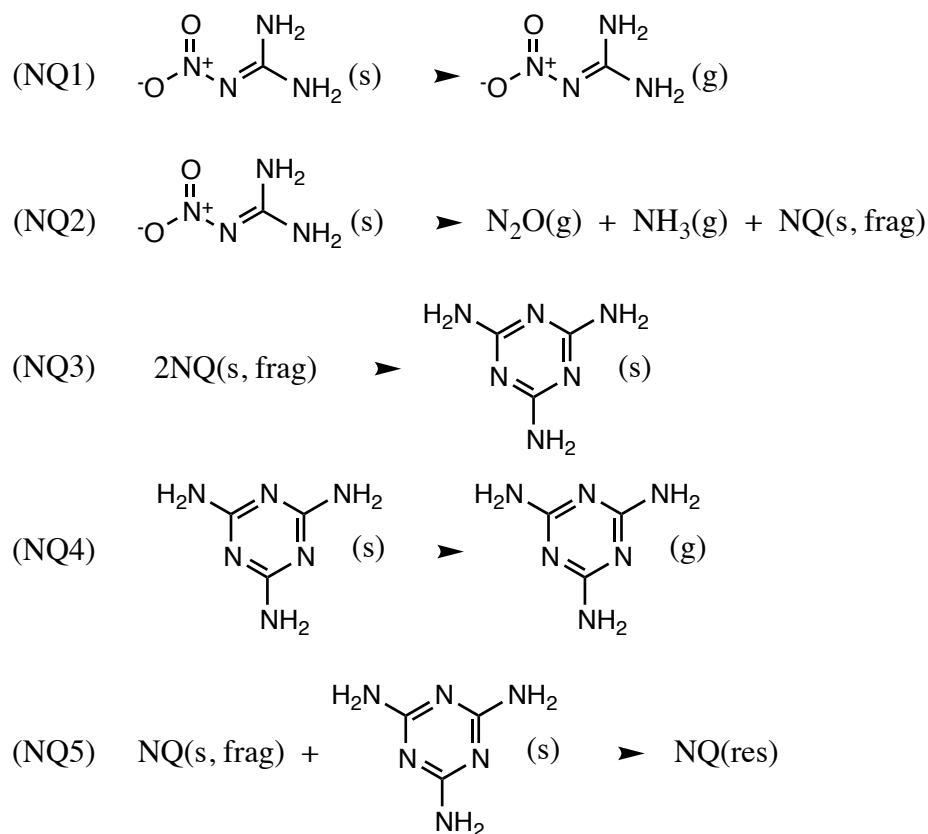


Figure 8. NQ thermal decomposition mechanism.

A more detailed discussion of the decomposition process for NTO has previously been presented [6]. In summary, NTO (see Figure 9) undergoes two competing reactions, an equilibrium sublimation reaction (NTO1) and bond-rearrangement NO elimination (NTO2) to form a reactive intermediate. The reactive intermediate decomposes through simple bond-rearrangement and bond-cleavage reactions to form the final HCNO , CO , N_2 , and NH_3 products (NTO3). A CNO oligomer also forms polymerizes into the final solid-phase residue. The observation that the final residue has a similar shape as the starting NTO indicates the decomposition process did not possess a liquid-phase process, but reacted strictly in the condensed-phase. Finally, the color and low density (7% residue) of the residue would indicate an unsaturated polymeric final product formed from the CNO oligomer chain.

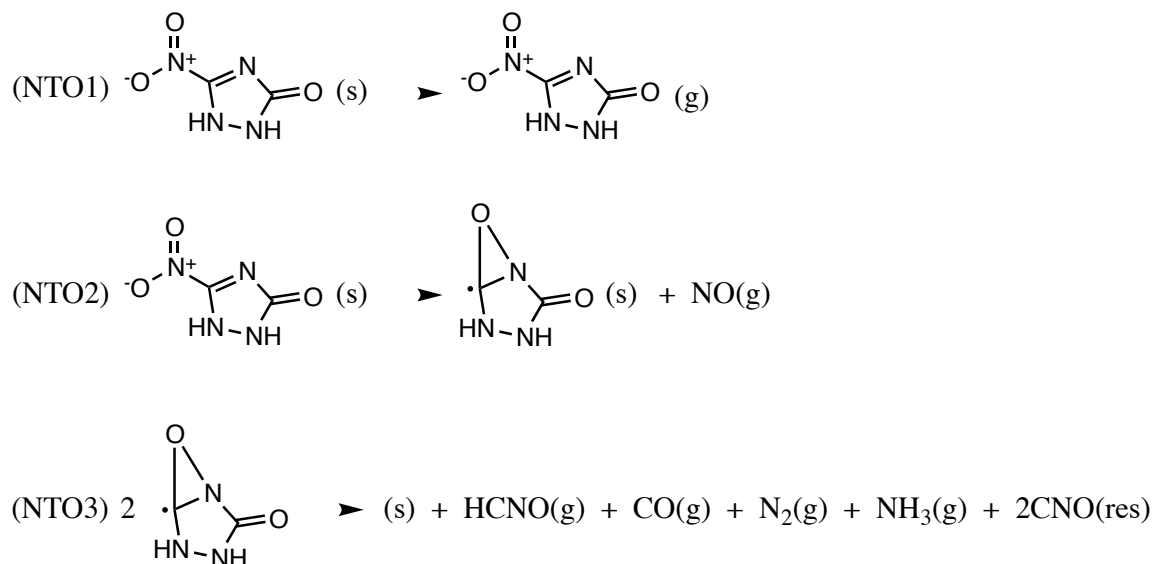


Figure 9. NTO thermal decomposition mechanism.

4.1. Reaction Mechanism

Decomposition of IMX-101 (see Figure 10) begins with low-temperature dissolution of some of the solid NQ into liquid DNAN (IM1). A mass transport process mixes the NQ/DNAN with the bulk liquid-phase DNAN and provides intimate contact between NQ and NTO particle surfaces. At the contact surface, NQ becomes adsorbed onto the NTO surface (IM2). Dissolved NQ also reacts directly in the dissolved state to form its normal decomposition products (IM3), while the surface reaction of NQ with NTO forms NQ and NTO decomposition products (IM4). Finally, the NQ/DNAN solution reacts with remaining liquid-phase DNAN to form a polymeric intermediate (I5) that can react with the NTO polymeric intermediate to form the final residue observed in figure 5. The main drivers for this altered reaction scheme is the dissolution of NQ into liquid-phase DNAN.

The reaction scheme for IMX-101 shows that the dominant factor controlling the decomposition process is a shift in the normal decomposition temperatures for the main ingredients. This temperature shift is the result of a direct interaction between DNAN, NQ, and NTO that alters the decomposition of each ingredient. The main driver for the interaction has been determined to be dissolution of NQ in liquid DNAN and subsequent reaction of this mix on NTO particle surfaces. Lot-to-lot variations of ingredients or IMX-101 formulation showed no changes to this temperature shift, and were therefore eliminated as a root cause for the shift. This eliminated causalities 2 and 3 listed under hypothetical causes above. Causality 1 was eliminated based on the lack of any observable changes to the normal decomposition route in binary combinations of DNAN/NQ and DNAN/NTO, however, it was pointed out above that our binary pairs were simple mechanical mixes and not melt-cast.

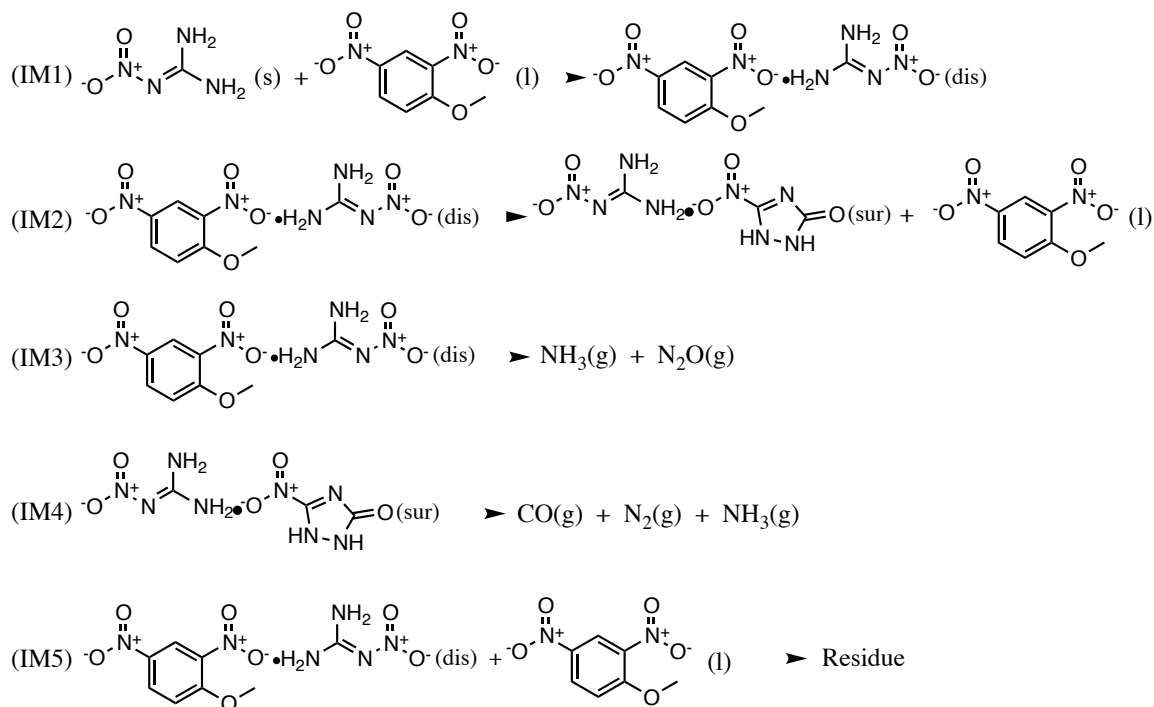


Figure 10. IMX-101 thermal decomposition mechanism.

4.2. Rate of Consumption of Reactive Solids

The low-temperature shifts in the onsets of decomposition for the IMX-101 ingredients raises the question of how much of each ingredient remains in the formulation when the normal decomposition temperature of each ingredient is reached. If the low-temperature shift allows substantial portions of the energetic solids to be consumed before the normal decomposition temperatures are achieved, the response of the material under the corresponding external stimuli would be expected to be relatively benign. Correspondingly, if no low-temperature shifts occurred, the majority of energetic solids would still be present when the higher decomposition temperatures are reached and the overall response for the non-interacting material would be relatively violent.

Figure 11 shows the rate of mass loss versus temperature curves for IMX-101 and Composition B. The IMX-101 mass loss results show that as the 215°C normal decomposition temperature for NTO is reached, well over 90% of the NTO has been consumed. In Comp B, the consumption rate of the energetic solid RDX is minimal before its normal decomposition onset temperature is achieved. For this formulation, predominantly all of the RDX remains when the higher temperature of its normal decomposition is achieved. The fully IM-compliant IMX-101 shows that response to external thermal stimuli that results in a shift of the decomposition to temperatures low enough that a substantial fraction of the energetic solids are consumed before their normal, violent, thermal response temperatures are reached. For Comp B, no such low-temperature shifts are observed, and the majority of the starting mass of the energetic solid RDX

is still present when its normal thermal response temperature is achieved, yielding an overall response that is more violent than with IMX-101.

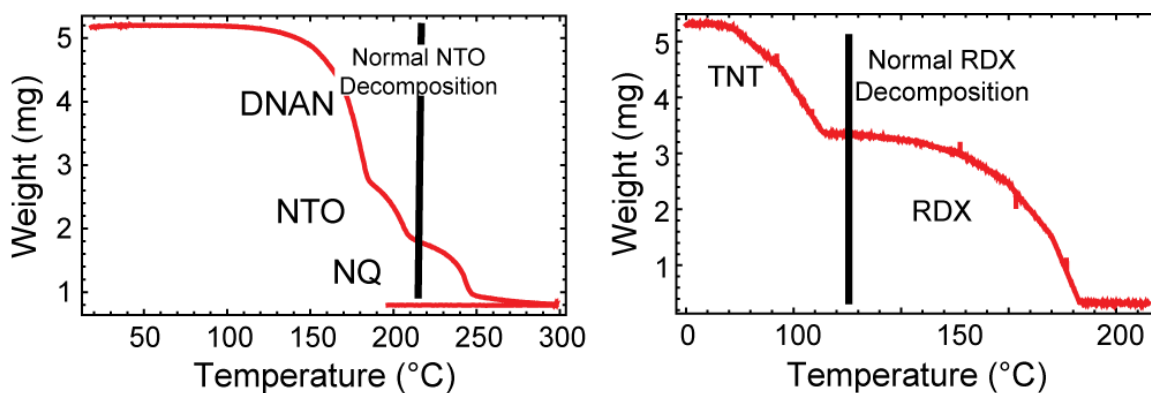


Figure 11. Mass loss versus temperature for IMX-101 and Composition B. The left panel shows the temperature dependent mass loss for the three ingredients in IMX-101, the vertical line indicates the onset of mass loss for NTO decomposition. The right panel shows the temperature dependent mass loss for the main ingredients in Comp B (TNT, RDX), with the vertical line showing the onset of mass loss for RDX.

These results indicate that the rate of consumption of the energetic solids in a formulation is an important factor. Based on this, an important property if IM compliance is the extent of consumption of each energetic solid in the formulation as well as the degree of decrease in the normal decomposition temperatures for said energetic solids. For formulations that are not IM compliant, reformulating the energetic solids with other ingredients to lower the normal decomposition onset temperatures of the energetic ingredients would allow the energetic solids to be consumed before their normal decomposition temperatures are achieved. This may provide a strategy for reducing sensitivity of other formulations by reformulation with slightly different ingredients.

5. CONCLUSIONS

We have conducted a series of STMBMS thermal decomposition experiments on IMX-101 and its ingredients. This formulation has been shown to be fully IM-compliant and this work was undertaken to gain a better understanding of the underlying reactive processes that control the response of IMX-101 to thermal stimuli.

Results show that a set of reactive processes occur in the full formulation that initiate decomposition of the main ingredients at temperatures well below the normal onset of decomposition. The dominant process is a low-temperature dissolution of NQ into liquid DNAN and subsequent deposition of NQ on NTO particle surfaces. Subsequent surface reactions occur at significantly lower temperatures than the normal bulk reactions and result in decomposition of the ingredients at significantly reduced temperatures than normally observed.

The shift to lower temperatures for the overall decomposition means that reactions are occurring at slower rates and material can be consumed under conditions where thermal transport within the material can still distribute energy before localized reaction hot-spots achieve thermal run-away. Therefore, the response of a material to an external energy stimuli can be seen as a balance between the rate of consumption of energetic solids and the thermal distribution of energy to prevent localized hot-spot formation. As the external event continues to drive energy into the material and increase its internal temperature, less and less energetic material is available to react and the overall response never rises to a violent event.

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