SAND2008-3058C

Reaction Mechanisms that Control the Thermal Decomposition Behavior of GUzT

Heather Hayden
Naval Surface Warfare Center, Indian Head Division
3817 Strauss Avenue
Suite 228, Bldg D323
Indian Head, MD 20640-5035

Richard Behrens and Deneille Wiese-Smith
Combustion Research Facility, Sandia National Laboratories
Livermore, CA 94551-0969

ABSTRACT

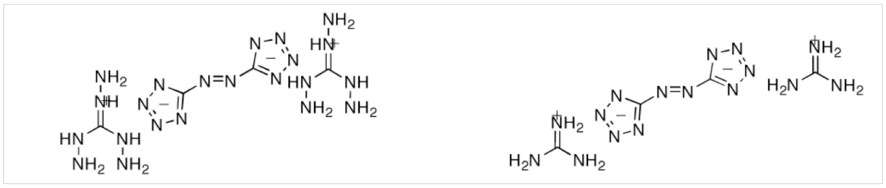
NSWC Indian Head is exploring the use of high nitrogen compounds such as Bis(triaminoguanidinium) 5,5'-azobitetrazolate (TAGzT) and Bis(guanidinium) 5,5'-azobitetrazolate (GUzT) TAGzT and GUzT as additives for propellant formulations not only for the purposes of burning rate modification but also as ingredients that may help existing and future formulations meet the demands of IM, safety and long-term aging requirements. From a performance perspective, TAGzT has proven significantly better at increasing the burning rate of RDX-based composite propellants than its similarly structured counterpart, GUzT. Previous thermal decomposition studies have shown that the hydrazine that is formed in the decomposition of TAGzT undergoes a very strong and rapid interaction with RDX. At temperatures near the melting point of RDX, the reaction rate of hydrazine with RDX is faster than the rate of decomposition of RDX by itself.

In order to determine why GUzT is less effective as a burning rate modifier in RDX-based composite propellants, simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and Fourier Transform ion cyclotron resonance (FTICR) mass spectrometry methods were used to examine the thermal decomposition of GUzT. Previous thermal decomposition studies show the decomposition of GUzT is a complex multi-step nonlinear process that predominantly involves the formation of volatile gases such as ammonia and nitrogen and a non-volatile residue that subsequently decomposes to form higher molecular weight products. This paper describes the next series of experiments conducted on GUzT using CoMPReHND, a new experimental paradigm that evaluates the various aspects of the important reactions identified in previous thermal decomposition studies. This new experimental protocol is being applied in order to gain further insight into the decomposition of GUzT and to investigate the thermal decomposition of GUzT over a range of conditions that are relevant to performance, safety and long-term aging behavior.

INTRODUCTION

In the quest to improve the performance of its gun systems, the Navy is exploring advanced propellant formulations. However, in addition to achieving higher performance objectives, the advanced propellant formulations must also meet insensitive munitions (IM), safety and aging requirements. High nitrogen compounds are being investigated as additives to existing formulations to meet these new requirements.

From a performance perspective, high nitrogen compounds such as TAGzT and GUzT are being investigated as additives to RDX-based composite propellants. Testing conducted at NSWC Indian Head shows that the burning rates of existing propellants are significantly altered when compounds containing high amounts of nitrogen are incorporated in the formulation[1]. Inspection of the data shows TAGzT has the most profound effect. TAGzT increases the burning rate of a typical RDX-based propellant by a significant amount. By comparison, GUzT, a similarly structured molecule (Figure 1) has little to no effect on the burning rate of typical RDX-based propellants.



Bis(triaminoguanidinium) 5,5'-azobitetrazolate(TAGzT) $C_4H_{18}N_{22}$

Bis(guanidinium) 5,5'-azobitetrazolate (GUzT) $C_4H_{12}N_{16}$

Figure 1 – TAGzT and GUzT Structures

Previous thermal decomposition studies have been conducted on mixtures of TAGzT and RDX in order to determine why TAGzT acts as a good burning rate modifier[2]. The results of the data show that the hydrazine that is formed in the decomposition of TAGzT undergoes a very strong and rapid reaction with RDX. At temperatures near the melting point of RDX, the reaction rate of hydrazine with RDX is faster than the rate of decomposition of RDX by itself. The main interaction between hydrazine and RDX involves the removal of the NO_2 groups from RDX and their reaction with hydrazine to form primarily H_2O, N_2O, CH_2NO and NO. The other gaseous products formed during the decomposition TAGzT - NH_3, HCN, and N_2 do not react with RDX to a significant extent when compared to the reaction of hydrazine with RDX. This study provided insight into the key features that are necessary for compounds to be good burning rate modifiers. Based on the study with TAGzT and RDX, the key feature of TAGzT that enables its interaction with RDX is the formation of hydrazine and its interaction with RDX.

In our initial work, the general features of the thermal decomposition behavior of GUzT were investigated[3]. During the thermal decomposition of GUzT, large quantities of ammonia are formed as opposed to hydrazine (which is formed from TAGzT), and this is likely the reason that little to no increase in burning rate is observed with GUzT modified propellant. However, in order to accurately address the issue of effective burning rate modifiers versus not so effective burning rate modifiers, the details of the decomposition of GUzT must be fully understood. Further, although GUzT may not be a candidate for burning rate modification, it may have properties that are more attractive from an IM, safety and/or long-term aging perspective. As such, a new experimental paradigm, “Concepts, Methods, and Protocols for Reaction Hierarchy and Network Development” (CoMPReHND)[4] is being applied in order to examine the reaction networks in more detail and to explore and ultimately characterize GUzT’s behavior over a broader range of experimental conditions. This, in effect, paves the way for the interactions between GUzT and RDX to be identified, probed and characterized.

METHODS

CoMPReHND has been used to determine the elements and linkages in the networks that control the thermal decomposition of GUzT. The instruments and methods used to conduct the thermal decomposition experiments are described elsewhere[5].

To determine whether GUzT is a candidate ingredient that will meet future munitions requirements, it is necessary to identify critical steps in the reaction network that determine the behavior of the ingredient under various lifecycle conditions. These include performance, manufacturability, safety and IM characteristics and long-term aging behavior.

From a performance perspective, TAGzT has proven to be more effective than GUzT when incorporated into propellant formulations[1]. Previous analysis has shown that hydrazine formed from the decomposition of TAGzT reacts more rapidly with RDX than RDX can decompose by itself[2]. Thus, compounds that decompose to form substantial amounts of hydrazine are likely to be good burning rate modifiers, if the hydrazine can survive the transport to a region in which it can encounter and react with RDX (or other nitramine compound). On, the other hand if hydrazine is formed, but undergoes secondary reactions prior to encountering RDX then it is not likely to be a good burning rate modifier. A previous thermal decomposition study conducted on GUzT[3] shows that is does not form hydrazine but instead predominantly forms ammonia during its decomposition. This is likely the reason that GUzT is not a good candidate for burning rate modification. The new experimental protocol addresses this issue with GUzT by probing the details of the processes (chemical and physical) associated with the decomposition of GUzT and answers the questions of how GUzT decomposes and what are the decomposition products that could interact with other ingredients.

Another key feature to consider in the analysis of GUzT is manufacturability and long-term aging. To be useful, compounds must be thermally stable. Compounds must be stable at the elevated temperatures often used in the manufacturing process. The new experimental protocol provides thermal decomposition data that allows for that determination by investigating and understanding the initial steps of the decomposition process as well as the cyclic processes within the reaction network that may have an "autocatalytic effect".

Safety and IM behavior is another critical area to consider in the analysis of GUzT. Compounds that form larger more stable molecules versus smaller gaseous molecules when they decompose are likely to be safer and more likely to meet IM requirements. In addition, compounds that alter decomposition process of RDX (or other nitramine ingredient) in such a way that it makes it less violent in cook-off or inhibits run-away of the reaction are valuable. The new experimental protocol is a tool which can be used to make that determination by looking at the IM and safety behavior of the compound individually, as well as in mixes with other ingredients.

In order to evaluate all the critical parameters mentioned above in one experiment, the temperature of a sample is varied over a temperature range from 20 to 500ºC in a controlled manner. The protocol is illustrated in Figure 2 with the data from the decomposition of a small sample of GUzT under low confinement conditions. The first set of heating and cooling steps is to identify the first steps in the decomposition process and determine the onset of decomposition. The next interval is a heat and hold section to determine if there is a delay associated with the onset of the secondary reactions. This provides insight into the complexity of the reaction process and whether the reaction network contains coupled reactions or feedback loops, which are often referred to as autocatalysis. The next section of temperature steps is to determine the onset of different secondary reactions in the network. This is followed by a series of heating and cooling cycles. This provides temperature dependent data on a sample whose characteristics are changing with time due to the complex reaction process occurring in the sample. Finally, the sample is heated to 500ºC to decompose any relatively non-volatile species that were formed during the decomposition process. This provides insight into the nature of the condensed phase species formed in the decomposition processes and allows closure on the elemental mass balance for quantification of the data. The details and the results of these experiments are discussed in the following section.

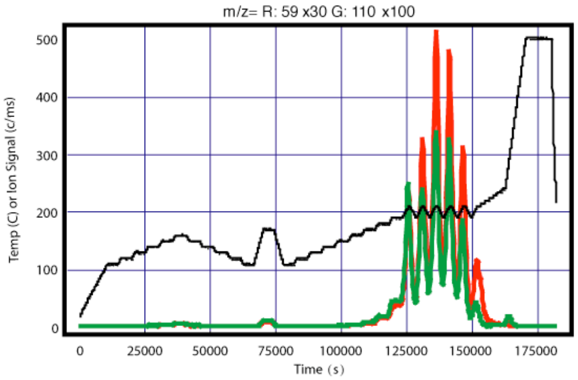


Figure 2. Illustration of experimental new protocol to examine critical features of GUzT decomposition

RESULTS AND DISCUSSION

Through the use of STMBMS and FTICR measurements of the products formed during the decomposition of GUzT, the general features of the physiochemical reaction process that control the decomposition of GUzT has been determined and previously reported[3]. The thermal decomposition of GUzT is complex and involves more than one process contributing to control the rate of decomposition. In addition, analysis of the data suggested that changes in the morphological features of the GUzT particles also affects the reaction processes. The decomposition products consisted of different gaseous products and a non-volatile residue that formed during the decomposition process and subsequently decomposed to form higher molecular weight products that evolved later in the experiment. A general reaction scheme that described the thermal decomposition of GUzT was created from the measurement of the decomposition products under low and high confinement conditions.

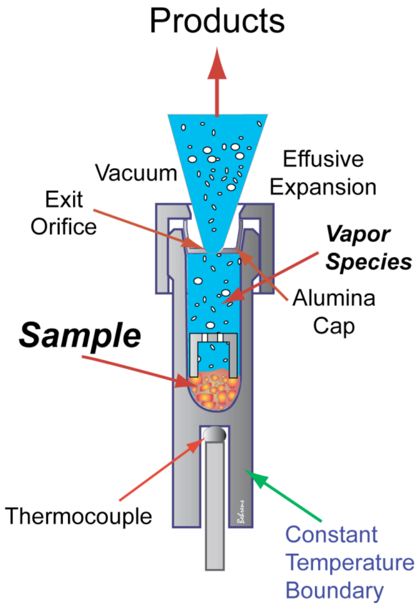


Figure 3. Cross section of reaction cell in STMBMS

More recent experiments conducted on GUzT using the new experimental protocol, led to the development and refinement of the existing reaction scheme of the thermal decomposition of GUzT. Two STMBMS experiments were conducted to explore the various important reactions associated with the decomposition of GUzT and to investigate the critical areas of interest including performance, manufacturing and long-term aging and safety and IM behavior. The complex heating profile described above was used for the two experiments under high and low confinement conditions. Both experiments used an ~2.0mg sample of GUzT. The reaction cell in the first experiment used an exit orifice diameter of ~1000μm, and the second experiment used an exit office diameter of 38μm. A cross section of the reaction cell used in the STMBMS experiments is shown in Figure 3. The data from the experiments illustrates how changes in the confinement of the gaseous decomposition products within the reaction cell are used to control the reaction process and provide further insight into these processes. From this, a more detailed and accurate reaction network can be developed to characterize the thermal decomposition of GUzT.

GUZT REFINED THERMAL DECOMPOSITION SCHEME

An updated and more refined reaction scheme that describes the thermal decomposition of GUzT has been created from the data from the next series of STMBMS and FTICR measurements. The updated reaction scheme of GUzT based on this data is presented in Figure 4. The reaction network is described first and then its various aspects are illustrated with the experimental results.

The first step involves the transfer of hydrogen from the guanidinium cation to the azobitetrazolate (ABT) anion resulting in the formation of gaseous guanidine and ABT (reaction R1). It is important to note reaction R1 is not written as though it were a reversible reaction. Close inspection of the data does not indicate that the GUzT is in dissociative equilibrium with its decomposition products. Future experiments will be conducted and may provide additional information about the equilibrium state of GUzT. However, based on the current data, some process occurring in the sample limits the reversibility of reaction R1.

Reaction R2 has been recently added to the GUzT thermal decomposition reaction scheme. It is written to capture the fact that guanidine is decomposing in the condensed phase and reacting to form a relatively non-volatile species, $C_3H_6N_6$ and gas-phase ammonia. This product being formed is most likely melamine, whose structure is shown in Figure 4. The data suggests higher confinement of the reaction cell will promote this reaction. Reaction R3 is written to capture the vaporization of melamine, which is the gaseous product measured at m/z value 126 in our experiments. The data suggests this reaction is more likely to occur in the low confinement experiment. Under low confinement conditions, the rate of evolution of melamine from the sample, which is in quasi two-phase equilibrium with the condensed phase, is more rapid due to the larger diameter orifice.

Reaction, R4 is written to capture the gas-phase decomposition of guanidine to form gas-phase ammonia, (NH_3) and an intermediate species measured at m/z value 42. This species has the molecular formula CH_2N_2. Two possible isomers are shown in Figure 4. The data suggests this is a reactive intermediate that forms higher molecular weight species. In addition, it is important to note the larger signal intensity of ammonia as compared to the species measured at 42 for both experiments. This would suggest if the CH_2N_2 species is not making its way out of the reaction cell, it might be predominantly reacting in the condensed phase.

R5 is another recently incorporated reaction. It is written to capture two possible pathways associated with the formation of the higher molecular weight, relatively non-volatile species, $C_3H_5N_5$. A possible structure is shown. The first possibility is “X” moles of guanidine react (in the condensed phase) with gas-phase HCN to form $C_3H_5N_5$

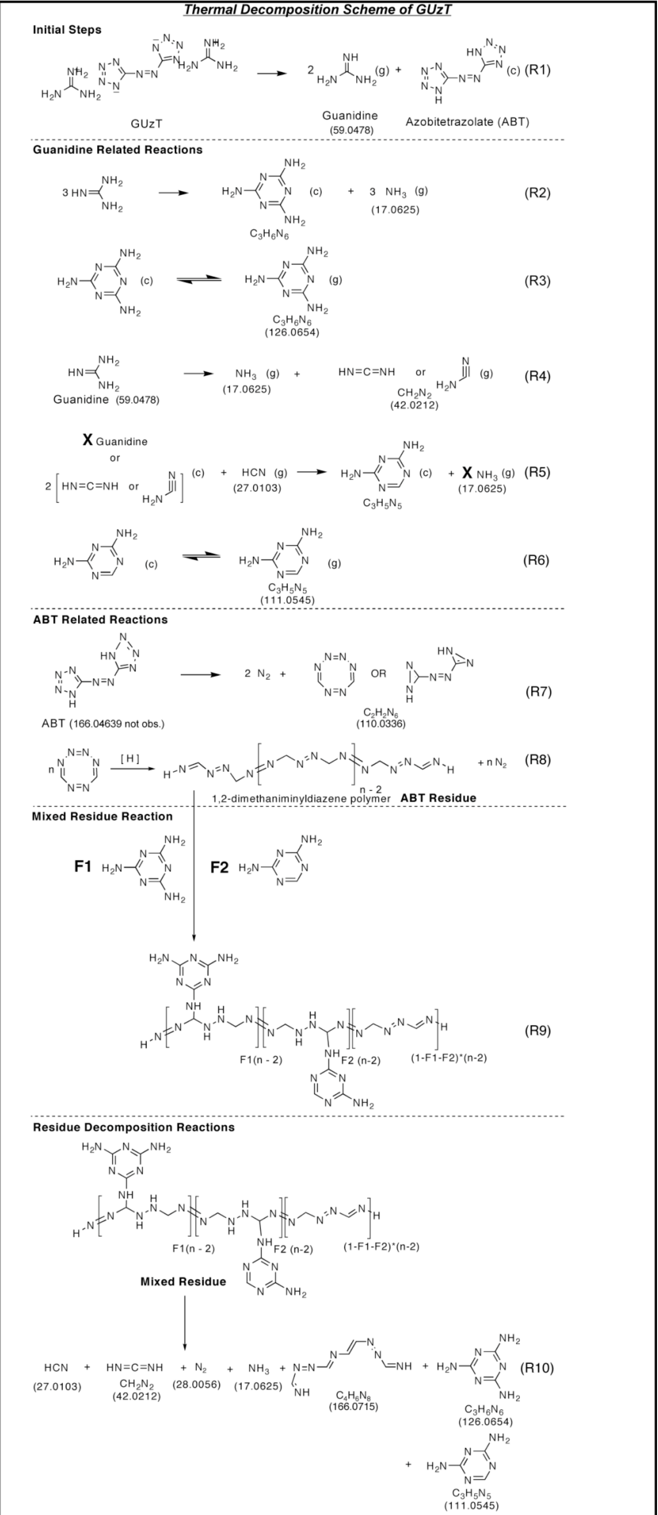


Figure 4. Reaction scheme representing the thermal decomposition of GUzT. Species listed with m/z values have been idenitified and their rate of evolution tracked during the course of each experiment.

and “X” moles of ammonia. The HCN originates from the decomposition of the mixed residue. The second possibility is two moles of the guanidine decomposition products (as shown in reaction R5) react with HCN to form $C_3H_5N_5$. Reaction R6 represents the vaporization of $C_3H_5N_5$ to form the gaseous product measured at m/z value 111. The data also suggests that this reaction is more likely to occur in the lower confinement experiment. The larger orifice allows the higher molecular weight gaseous species to exit the reaction cell more rapidly than in the higher confinement experiment.

R7 is a reaction that was present in the previous GUzT thermal decomposition scheme. It represents the decomposition of the molecule formed from the ABT. The molecular ion of ABT (m/z value 166) is not observed in the mass spectra, but the largest fragment of the ABT is observed at m/z value 110. It has the molecular formula $C_2H_2N_6$. This species originates from the central portion of the ABT molecule, the regions around the diazine group, and appears to be formed after the elimination of nitrogen from both rings. Two possible isomers of the $C_2H_2N_6$ species are shown.

Reaction R8 was also present in the previous thermal decomposition scheme. This reaction captures the fact that the 110 species is likely to form a non-volatile “polymeric-like” product (NVPP) or ABT residue during the decomposition of GUzT. The ABT residue has not been directly observed as of yet but the identities of the gaseous products that evolve, (a) after the GUzT is completely decomposed and (b) late in the experiment as the sample is heated to 500ºC, is consistent with this type of compound forming during the decomposition of GUzT.

Reaction R9 is written to capture the interaction occurring between guanidine and ABT residue. It is written to capture the fact that fraction (F1) of $C_3H_6N_6$ or fraction (F2) of $C_3H_5N_5$ is going to interact with the ABT residue. As mentioned earlier, reactions R3 and R6 represent the vaporization of the larger molecular weight species, $C_3H_5N_5$ and $C_3H_6N_6$. Under lower confinement, these species escape faster due to the higher flow rate out of the larger orifice, given the constant pressure of these species established by the two-phase equilibrium in the reaction cell. Under higher confinement these species are confined within the reaction cell in larger amounts and for longer periods of time. Thus, reaction R9 is more likely to occur. The ABT residue interacts with and absorbs the products, forming the mixed residue shown in reaction R9.

Reaction R10 represents the decomposition of the mixed residue. In both experiments, as the sample is heated to 500ºC the prominent gaseous decomposition products include, HCN, N_2, CH_2N_2 (42), $C_3H_5N_5$ (111), $C_3H_6N_6$ (126) and $C_4H_6N_8$ (166). It is important to note an observation made about the product measured at m/z value 111 in the high temperature region. Under low confinement, the product at m/z value 111 tracks the temporal behavior of the product measured at m/z value 126. This would suggest 111 is a daughter ion of the larger 126 molecule formed in the mass spectrometer. However, in the high confinement experiment, the temporal behavior of 111 and 126 are different. As such, it is likely the product measured at 111 has two sources; (1) fragmentation of the 126 molecule in the mass spectrometer and (2) the decomposition of the residue formed during the decomposition of GUzT.

The refined reaction scheme that captures the dominant features of the decomposition of GUzT has been presented and the analysis is based on the data that follows.

TEMPORAL BEHAVIOR OF THE RATES OF REACTION

Our recent experiments further confirm that the thermal decomposition of GUzT involves complex, multi-step, nonlinear reaction processes and were used to create the reaction network shown in Figure 4. The data were collected from both low and high confinement experiments, where the sample is heated over a wide range of temperatures. Three regions of the experiments are analyzed, and comparisons of the temporal behavior of the ion signals are made. The three regions of the experiment investigated include the low temperature region, a thermal cycling region and a high temperature range where the sample is heated to 500ºC.

The new experimental protocol provides data to determine the reaction that initiates the decomposition of GUzT and provides data that helps determine how fast this occurs as a function of temperature. The data illustrating this feature for GUzT is shown in Figure 5. The ion signal data representing these species formed under low confinement and at lower temperatures are shown in the two graphs located on the left and the corresponding ion signals for the experiment conducted under higher confinement are located on the right. The first set of experiments involving heating the sample to 160ºC and cooling it back down is performed to identify the first steps in the decomposition process and determine the onset temperature of decomposition. For GUzT, the initial reaction involves the decomposition of GUzT to form gas-phase guanidine and ABT. This is represented by reaction R1 in the GUzT decomposition reaction scheme (Figure 4). In our experiments, the onset of GUzT decomposition is observed at 140ºC under lower confinement (Graph [1,1] of Figure 5) and at 150ºC (Graph [1,2]) under higher confinement. The guanidine that evolves from the sample is represented by ion signals at m/z value 59 and 43. 59 is the molecular ion of guanidine and 43 is a daughter ion in its mass spectrum.

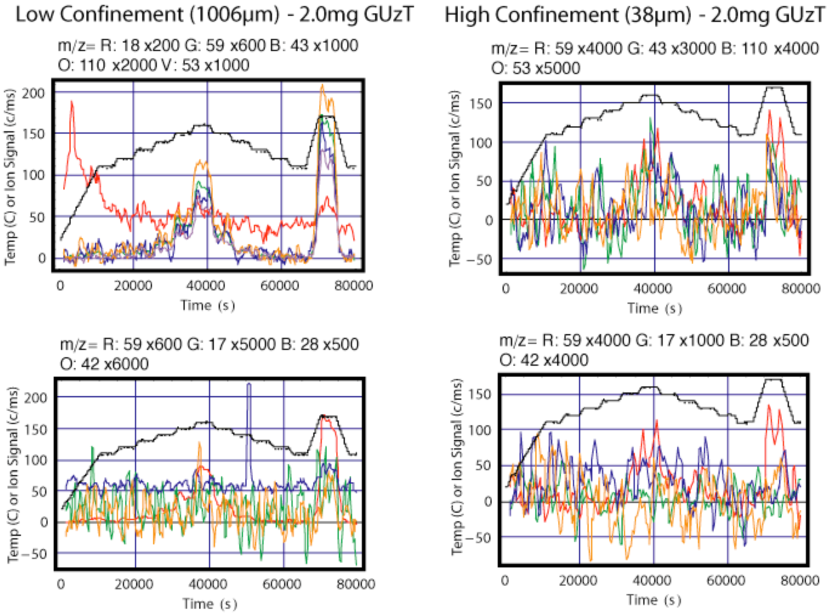


Figure 5. Comparison of ion signals representing different products evolving during the thermal decomposition of GUzT at lower temperatures. The color codes for m/z values and scaling factors are listed at the top of each graph.

According to the data in Figure 5, the first steps in the decomposition of GUzT also include the product associated with the decomposition of ABT (reaction R5). This product also starts to evolve at 140ºC in the low confinement experiment (Graph [1,1]) and at 150ºC in the high confinement experiment (Graph [1,2]). The most abundant ABT decomposition product is represented by ion signals at m/z values 110 and 53. 110 is not the molecular ion of ABT but represents the largest fragment of ABT. 53 is a daughter ion in its mass spectrum. Further inspection of the low confinement data shows the rate of evolution of the product at 110, tracks that of the gas-phase guanidine. In both experiments, the rates of evolution of the products are small but significant as the sample is heated to 160ºC.

Also included in the data in Figure 5 (Graph [1,1]) is the ion signal measured at m/z value 18. Inspection of the data shows that water evolves from the sample as the sample is heated from 20 to 110ºC in both the high and low confinement experiments.

The next heating interval shown in Figure 5 is the ramp from 110ºC to 170ºC. This is a heat and hold section to determine if there is a delay time associated with the onset of the secondary reactions. This provides insight into the complexity of the reaction process and to determine whether the reaction network contains coupled reactions or feedback loops (often referred to as autocatalysis). The low confinement data primarily provides the information with respect to the secondary reactions. In the low confinement experiment, the first evidence of the decomposition of guanidine appears. The decomposition of guanidine (reaction R2) forms the volatile products ammonia (NH_3) and carbodiimine or cyanamide (CH_2N_2). The possible isomers of CH_2N_2 are represented by the signal measured at m/z value 42 and ammonia is represented by the signal at m/z value 17. Graph [2,1] in Figure 5 shows that as the sample is heated to 170ºC the products associated with the decomposition of guanidine (17 and 42) start to appear. This is also the temperature where nitrogen, which is associated with the decomposition of ABT (reaction R7), first appears. Nitrogen is represented by the signal at m/z value 28. (It is important to note, background at m/z value 28 indicates there is a small air leak in the STMBMS instrument). However, since the ion signals that represent the decomposition of guanidine are small it is difficult to conclusively determine if there is a delay time associated with the onset of the secondary reactions from this data. Future experiments may provide additional information about this particular behavior in this temperature region.

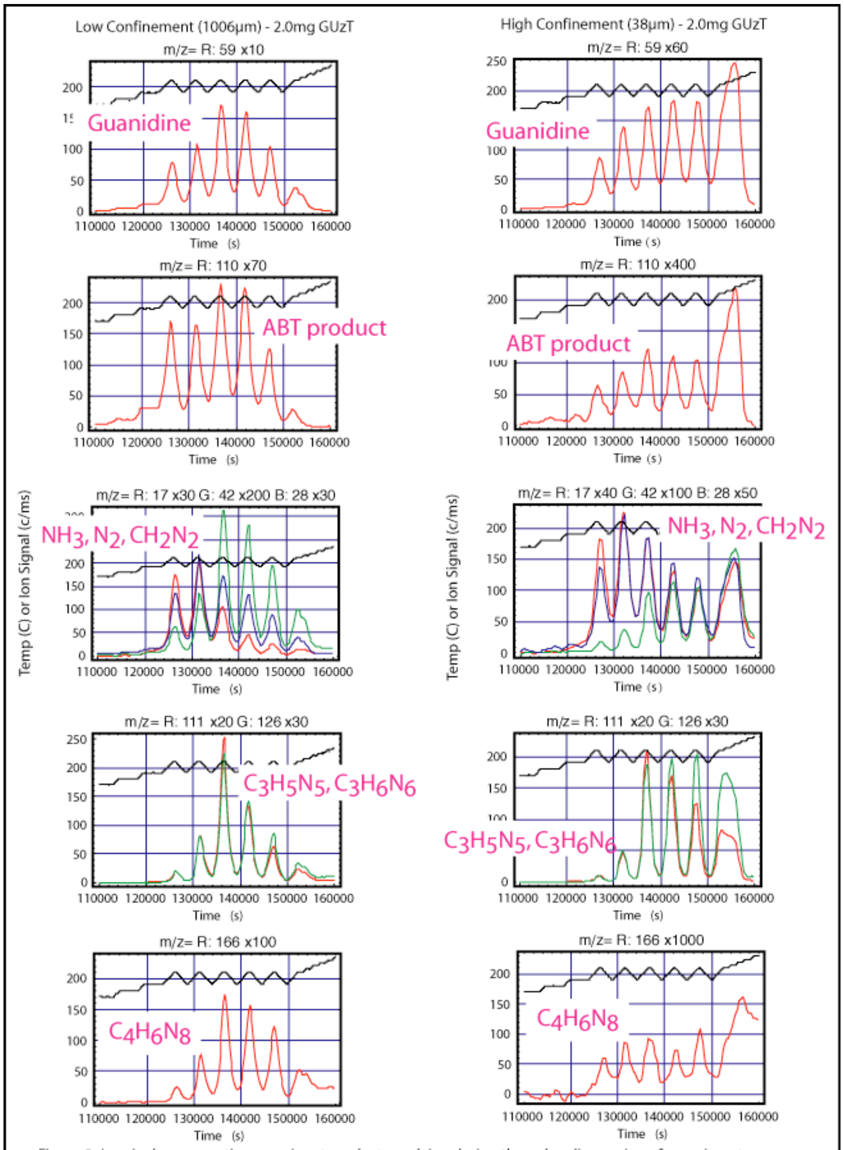


Figure 6. Ion sigals representing prominent products evolving during themal cycling region of experiments.

The complex behavior that controls the decomposition of GUzT between low and high confinement conditions is investigated with a series of heating and cooling cycles from 190 to 210ºC. This provides temperature-dependent data on the GUzT sample whose characteristics are changing with time due to the complex reaction process occurring in the sample. This data is illustrated in Figure 6. The graphs in the left column show the rates of evolution of the major decomposition products of GUzT through thermal cycling and into the first few isothermal steps for the lower confinement experiment. The graphs in the right column show the rates of evolution of the same products, in the same region, for the higher confinement experiment. The major products evolving during the thermal cycling region are represented by the ion signals at the following m/z values: guanidine - CH_5N_3 (59), NH_3 (17), CH_2N_2 (42), $C_2H_2N_6$ from ABT (110), N_2 (28), C_3H_6N6 (126), and $C_3H_5N_5$ (111).

The data in Figure 6 illustrates how changing the extent of the confinement of the gaseous species controls the reaction process. Comparison of the intensities of the ions signals of the various species under low and high confinement shows higher confinement promotes contributions from reactions that are strongly affected by secondary reactions (i.e., R2, R4 and R9) and reduces contributions from species that either undergo further reactions (e.g., guanidine) or are in quasi two-phase equilibrium (e.g., species represented by m/z values 111 and 126).

Inspection of the data from both high and low confinement experiments shows an increasing rate of evolution of guanidine (Graph [1,1] and [1,2]) during each subsequent heating and cooling cycle. This behavior does provide evidence that the decomposition of GUzT consists of a feedback loop where products formed early in the process accumulate and lead to an increasing rate of reaction as the experiment progresses. However, in the lower confinement experiment, the rate of evolution of guanidine is higher than in the higher confinement, but starts to decrease prior to the last cycle. In the high confinement experiment, the rate of evolution of guanidine continues to increase throughout the cycling region. These differences suggest that in the low confinement experiment, more of the guanidine leaves the reaction cell and less undergoes secondary reactions. In contrast, under higher confinement the net rate of decomposition of GUzT is slower (possibly due to the reversibility of reaction R1) which is slowed by the lower rate of evolution of guanidine from the reaction cell. However, higher confinement of the gases leads to a more substantial increase in the rate of evolution of several products during each subsequent cycle.

In our experiments, the rate of evolution of the product associated with the decomposition of ABT, the product represented by ion signal 110, is generally consistent in the higher confinement experiment with only a slight increase through the first two cycles. The low confinement experiment shows a larger increase in the rate of evolution through the first three cycles and then decreases more dramatically as the cycles are completed. The rate of evolution of the ABT decomposition product is almost two orders of magnitude higher in the low confinement experiment than in the higher confinement experiment. This is consistent with the product undergoing more secondary reactions within the reaction cell.

Graphs [3,1] and [3,2] show the temporal behavior of the ion signals at m/z values 17, 28 and 42 for each experiment through the thermal cycle. NH_3 (17) and CH_2N_2 (42) are the volatile species associated with the decomposition of guanidine and N_2 (28) is the product formed as ABT decomposes. The rates of evolution of NH_3 and N_2 exhibit similar behavior between the two experiments; changes in confinement do not appear to affect the rates substantially. However, the rate of evolution of CH_2N_2 is somewhat different between the two experiments. In the low confinement experiment, there is a dramatic increase in its rate of evolution, which subsequently decreases as the cycles are completed. However, in the high confinement experiment, the rate of evolution of CH_2N_2 gradually increases through the course of the thermal cycles. This behavior is similar to what was observed with guanidine, and the same argument applies as to the differences in the behaviors between experiments. It is also important to note there is significantly less CH_2N_2 gaseous product evolving as compared to NH_3 in both experiments. This is consistent with the reaction of the intermediate in the condensed phase (as reflected in R5 in the reaction scheme in Figure 4) to likely form the higher molecular weight products.

Two of the dominant higher molecular weight products formed from the decomposition of GUzT are $C_3H_5N_5$ (111) and $C_3H_6N_6$ (126). The rates of evolution of the two products are shown in Graph [4, 1] and [4, 2] in Figure 6. The temporal behavior of the two products is consistent from one experiment to the next during the first three cycles. This rapid increase in the rate of evolution of the products is also consistent with the conclusion that the decomposition of GUzT consists of a feedback loop, where products formed early accumulate and lead to an increasing rate of reaction. Further, the changes in confinement suggest that the products being formed are evaporating and escaping from the reaction cell in the low confinement experiment, whereas in the high confinement experiment, the increased frequency of secondary reactions leads to formation of greater amounts of residue. Closer inspection of the temporal behavior of the ion signals for $C_3H_5N_5$ and $C_3H_6N_6$ also supports the idea that the formation of these products occurs in the condensed phase. If these products were forming in the gas phase, their signals would be proportional to the guanidine ion signal. Comparison of the guanidine signal with $C_3H_5N_5$ (111) and $C_3H_6N_6$ (in both experiments) clearly show this is not the case. As such, this is consistent with the postulated reactions R2 and R5 in the reaction mechanism.

The decomposition product measured at 166 has the molecular formula $C_4H_6N_8$ and its behavior is illustrated in Graph [5, 1] and [5,2] in Figure 6. The data shows the same rapid increase in rate of evolution in the low confinement experiment through the first two cycles and a more gradual rate of evolution in the high confinement experiment through all the cycles. In addition, the rate of evolution of $C_4H_6N_8$ is approximately one and a half orders of magnitude larger in the low confinement experiment than in the high confinement experiment. This also illustrates the extent to which changes in confinement control the reaction processes.

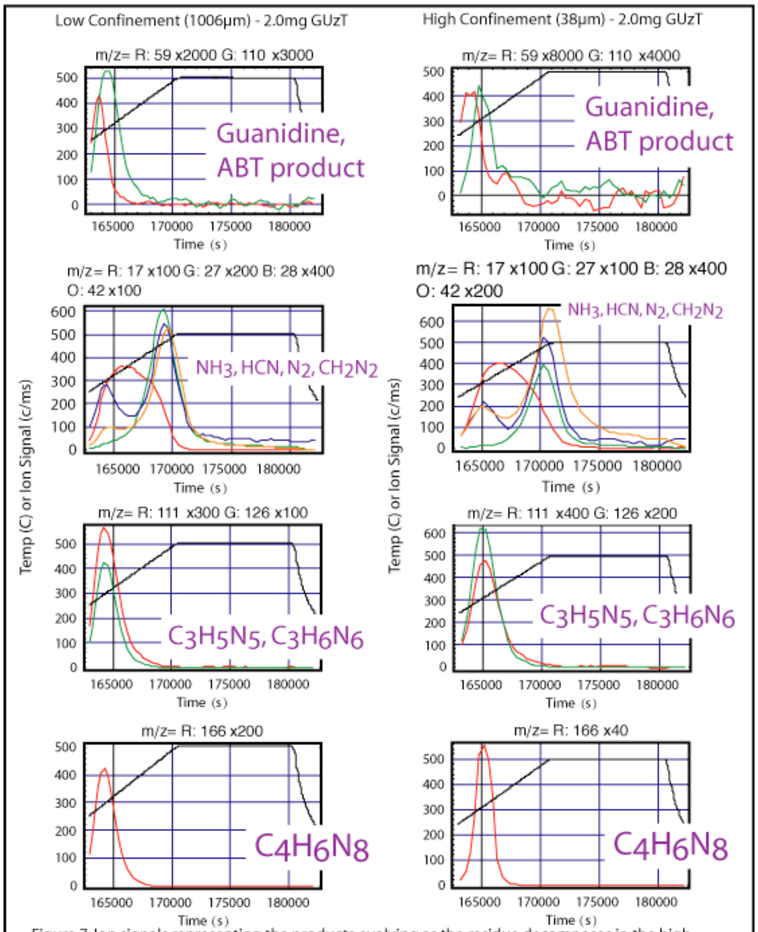


Figure 7. Ion signals representing the products evolving as the residue decomposes in the high temperature heating range.

As summarized in the reaction network, the decomposition of GUzT involves complex reactions that occur in the condensed phase as well as in the gas phase. This leads to the formation of a non-volatile residue (NVR) during the decomposition of GUzT. In order to investigate the residue that forms, the final stage of the experiment includes heating the sample to 500ºC to decompose the NVR formed during the GUzT decomposition process. This provides insight into the nature of the condensed phase species formed in the decomposition processes, and allows closure on elemental mass balance for quantification of the data. This data is illustrated in Figure 7. The graphs in the left column show the rates of evolution of the major decomposition products of the residue that is formed during the decomposition of GUzT under low confinement. The graphs in the right column show the rates of evolution of the same products, in the same regions, for the high confinement experiment.

The major products that evolve as the NVR is heated from 240 to 500ºC are NH_3 (17), HCN (27), CH_2N_2 (42) and melamine (126). Lesser amounts of N_2 (28), guanidine (59), ABT (110), and $C_3H_5N_5$ (111) are also observed. Interestingly, the portion of the NVR that is formed from the backbone of the ABT and evolves during its decomposition (m/z value 166) is fives times greater under high confinement conditions. Close examination of the evolution sequence of the products reveals a behavior that is consistent with the structure of the residue postulated as being formed via reactions R8 and R9. The first species to evolve are NH_3 (17), melamine (126) and $C_3H_5N_5$ (111). Ammonia evolves over a relatively broad temperature range (~250 to 500ºC) and most likely originates from the decomposition of melamine (126) or $C_3H_5N_5$. The melamine and $C_3H_5N_5$ evolve over a narrower temperature range (~250 to 400ºC), which coincides with the evolution of the $C_4H_6N_8$ that most likely originated from the reactions of ABT via reaction R8. At higher temperatures, the main species to evolve are HCN, N_2 and CH_2N_2. These are likely to evolve from the decomposition of the backbone of the NVR as shown in reaction R10. The identities of the products and the sequence of their evolution from the samples were used to construct the portion of the reaction network characterized by reactions R8 through R10.

SUMMARY AND CONCLUSIONS

NSWC Indian Head is exploring the use of high nitrogen compounds additives for propellant formulations not only for the purposes of burning rate modification but also as ingredients that possibly help existing and future formulations meet the demands of IM requirements. From a performance perspective, TAGzT has proven significantly better at increasing the burning rate of RDX-based composite propellants than its similarly structured counterpart, GUzT.

Simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and Fourier Transform ion cyclotron resonance (FTICR) mass spectrometry methods are being used to further examine the thermal decomposition of GUzT. Previous thermal decomposition studies show the decomposition of GUzT, is a complex multi-step nonlinear process that predominantly involves the formation of volatile gases such as ammonia and nitrogen and a non-volatile residue that subsequently decomposes to form higher molecular weight products.

The next series of experiments conducted on GUzT uses CoMPReHND, a new experimental paradigm, that evaluates the various aspects of the important reactions identified in previous thermal decomposition studies. A new experimental protocol is being applied to gain further insight into the decomposition of GUzT and to investigate the thermal decomposition of GUzT over a range of conditions that are relevant to performance, safety and long-term aging behavior.

A refined reaction scheme describing the thermal decomposition of GUzT has been developed based on the results of the current experiments. Two experiments were conducted at high and low confinement over a wide range of temperatures. The initial steps of the decomposition of GUzT were investigated by heating the sample in steps to 160ºC, cooling it back down to 110ºC and then heating is again to 170ºC. The sample was then heated and cooled through a series of thermal cycles, which explored the temperature dependence of the different reactions controlling the thermal decomposition of GUzT. Finally, in order to investigate the decomposition of the NVR that forms during the decomposition of GUzT, the sample was heated to 500ºC. The data from these experiments were used to further develop the GUzT thermal decomposition reaction scheme.

The reaction network that characterizes the decomposition of GUzT consists of ten reactions. During the thermal decomposition of GUzT, gaseous products evolve, a residue forms and the residue that forms also subsequently decomposes.

The first reaction pathway is the decomposition of GUzT to form gaseous guanidine and ABT. There is a transfer of a proton from the guanidinium cation to the azobitetrazolate anion that appears to be the first step ion the process.

The second reaction represents the decomposition of guanidine in the condensed phase to form the higher molecular weight species melamine ($C_3H_6N_6$) and ammonia. This product although it is made early in the process accumulates in the NVR and its rate of evolution increases as its mole fraction in the condensed phase builds during the course of the experiment. Reaction R3 represents the vaporization of the melamine. This species is measured at m/z value 126. The data clearly shows that the changes in confinement effect whether it simply evaporates or interacts with the residue.

The fourth reaction represents the decomposition of gas-phase guanidine to form ammonia and the CH_2N_2 isomer. Both of these products are measured in the mass spectrometer. However, the stronger intensity of the ammonia signal as compared to the CH_2N_2 signal suggests that the CH_2N_2 isomer reacts to form condensed phase products.

Reaction R5 represents the interaction of guanidine or its decomposition products with gas phase HCN to form the species, $C_3H_5N_5$ and ammonia. The HCN comes from the decomposition of the mixed residue that forms. Reaction R6 represents the vaporization of the condensed phase species $C_3H_5N_5$. This species is measured in the mass spectrometer at m/z value 111. As was the case with the species formed in Reaction R3. The data suggests that this reaction also is more likely to occur in the low confinement case.

Reactions R7 and R8 represent the ABT related reactions. The ABT molecular species is not observed during the decomposition process. The main products formed from the decomposition of ABT are N_2 and a species with a molecular weight of 110, which has the formula $C_2H_2N_6$. This species originates from the central portion of the ABT molecule. This central portion also reacts to form a residue. Reaction R8 captures that process. It has not been directly observed, but the identities of the gaseous products that evolve as the sample is heated to 500ºC and after the GUzT has completely decomposed, suggest that this type of compound is formed.

Reaction R9 represents the interaction of the guanidine residue and the ABT residue to form a product identified in the reaction scheme as the mixed residue. This reaction is more likely to occur in the high confinement experiment. In the high confinement experiment, the data suggests that the products that are formed earlier in the experiment, $C_3H_5N_5$ and $C_3H_6N_6$ do not readily evaporate as was expressed by R3 and R6. Instead, they interact with the residue that has formed from the ABT. This interaction causes a mixed residue to form. This reaction is written to capture the fact that some fraction of either of the species is likely absorbed by the residue.

Reaction R10 is the final reaction pathway and represents the decomposition of the residue that is formed from reaction R9. The prominent products evolving as the residue decomposes are NH_3 (17), CH_2N_2 (42), HCN (27), N_2 (28), C_3H_6N6 (126), $C_3H_5N_5$ (111) and $C_4H_6N_8$ (166).

As mentioned earlier, test data collected at NSWC Indian Head shows that incorporating TAGzT into propellant formulations significantly alters the burning rate of a nitramine propellant. However, its similarly structured counterpart GUzT does not. Although the decomposition of the two materials is similar in that there are complex, non-linear, physiochemical processes controlling the decomposition of the compounds, the glaring difference between the two materials is the fact that significant amounts of hydrazine form during the decomposition of TAGzT while mostly non-volatile products, like ammonia are formed from the decomposition of GUzT. This is likely the reason GUzT is not an effective burning rate modifier. However, from the analysis presented in this paper, there are still several features of the GUzT decomposition process that may provide for interactions with typical propellant ingredients like RDX: (1) reactions with one or more of the major gas phase products, NH_3 (17), CH_2N_2 (42), N_2 (28), C_3H_6N6 (126), or $C_3H_5N_5$ (111), or (2) interaction of RDX with the non-volatile residue products that are being formed. The interaction of GUzT and RDX is currently being investigated using the CoMPreHND method and the STMBMS and FTICR instruments. Although, there is no hydrazine formed from the decomposition of GUzT, preliminary results show GUzT significantly alters the decomposition behavior of RDX.

Even though GUzT is not an effective burning rate modifier, the results of this analysis suggest there are other aspects of GUzT that may make it a good candidate from an IM, safety or long-term again perspective. It appears to be more thermally stable. Its initial decomposition occurs at higher temperatures. This is important from a manufacturing perspective and it may not have compatibility or safety issues that other compounds possess. Further, the larger more stable molecules that form during the decomposition of GUzT may make it safer and more likely to meet IM requirements.

FUTURE WORK

The results presented in this paper cover our analysis of the thermal decomposition of GUzT using the new experimental paradigm CoMPReHND. To build on this effort, further work will be conducted in the following areas, (1) refinement of the mechanisms that describe the decomposition of GUzT by conducting medium confinement experiments, (2) quantification of the decomposition processes and development of mathematical models to describe the reaction processes that control the decomposition of GUzT, (3) investigation of the reactions of GUzT with RDX, (4) investigation of the reaction of GUzT with other types of nitramines and the ingredients used in propellant binders and (5) the examination of propellant formulations containing GUzT.

ACKNOWLEDGEMENTS

This work is supported in part by a memorandum of understanding between the DoD Joint Munition Program and the DOE, the Office of Naval Research and the Army Research Office under contract 43381-CH. We thank Aaron Highly and Sean Maharrey for assistance collecting the FTICR data. Heather Hayden thanks Dr. Christine Michienzi from NWSC Indian Head for technical guidance and Prof. David Chichka, Prof. Charles Garris and Merrill King for their support and participation in her research advisory board as representatives from George Washington University in Washington, D.C.

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