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REACTION PROCESSES THAT CONTROL THE THERMAL DECOMPOSITION OF MIXTURES OF TAGZT AND RDX

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

Heather Hayden
Naval Surface Warfare Center, Indian Head Division
101 Strauss Avenue
Indian Head, MD 20640-5035

ABSTRACT

To determine why TAGzT acts as a good burn 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 mixtures of bis(triaminoguanidinium) 5,5'-azotetrazolate (TAGzT) and hexahydro-1,3,5-trinitro-s-triazine (RDX). 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 and N_2O. The other gaseous products formed during the decomposition of 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. Since the reaction of hydrazine with RDX is rapid compared to the decomposition of RDX alone, compounds that decompose to form hydrazine at a temperature near the decomposition temperature of the nitramine ingredient should be good candidates for burn rate modifiers for nitramine-based composite propellants.

INTRODUCTION

Munition systems of the future will be required to achieve new performance objectives while meeting insensitive munition (IM), safety, environmental compliance, and health requirements. Performance objectives will require increasing the energy deposited on target, and doing it in controlled and field-tailored manner. This will require chemical propulsion systems with features that go beyond current design capabilities. Meeting these objectives will require new solid propellants whose combustion behavior can be tailored to meet specific needs.

For example, in a quest to improve the performance of its gun systems, the Army and Navy are exploring advanced propellant formulations. Tailoring the burn rate of nitramine propellants through the use of high-nitrogen energetic compounds is an approach to achieve that goal. The advantage is an increase in the energy or work delivered to the projectile that won't exceed the hardware limitations of the gun system. Studies conducted using this system show that a potential 92% increase in range could be achieved.[1] High nitrogen compounds are also attractive in that they have high heats of formation, they lower the flame temperature of propellants and their high nitrogen content is favorable for mitigating gun barrel erosion.[2-4]

High performance, smokeless propellants often employ nitramines, such as RDX, as a primary ingredient. While nitramines provide significant energy enhancements in solid propellants, until recently there has been little success in developing burn rate modifiers that can be used to tailor their combustion behavior to meet more demanding design requirements. The conventional formulation and test methods used to development burn rate modifiers for double-base propellants have been unsuccessful, when applied to nitramine-based propellants.[5]

In the Navy's program to examine the use of high-nitrogen compounds to develop advanced gun propellants, closed bomb combustion results revealed that triaminoguanidinium azotetrazolate (TAGzT) significantly increases the burn rate of the nitramine-based propellant, EX-99 (76.0% RDX, 12.0%CAB, 4.0%NC, 7.6%BDNPA/F, 0.4%EC).[1, 6] This result shows that TAGzT can be an effective burn rate modifier for nitramine-based propellants.

If an understanding of why TAGzT is an effective burn rate modifier can be determined, then this information may be used to guide the design of other molecules with a range of different properties that may also be effective burn rate modifiers.

To address this issue we examined the interaction of TAGzT, RDX and their decomposition products to determine (1) whether the decomposition behavior of RDX is altered by the presence of TAGzT and (2) if it is, the nature of the underlying reaction process that controls the interaction.

<u>RDX Decomposition</u>. Previously, we have examined the decomposition of RDX[7-11] and TAGzT[12]. The reaction process that controls the decomposition of RDX is nonlinear and complex. This behavior is illustrated in Figure 1 by the different temporal behaviors of the rate of formation of the products formed during its decomposition. For example, the rate of evolution of RDX increases as the sample melts (~200°C). As the sample melts there is a rapid increase in the rate of formation of oxy-s-triazine (OST), which is formed via the direct decomposition of RDX. In contrast, many of the decomposition products (e.g., CH_2O and N_2O), formed via the mononitroso intermediate of RDX, hexahydro-1-nitroso-3,5-dinitro-s-triazine (ONDNTA), appear later in the decomposition process. A non-volatile residue (NVR) also forms during the decomposition process. Once NVR has formed, it too reacts directly with RDX, opening new reaction pathways. Some features of the NVR have been determined by monitoring the gaseous products formed as the NVR decomposes (e.g., trimethylamine, $(CH_3)_3N$).

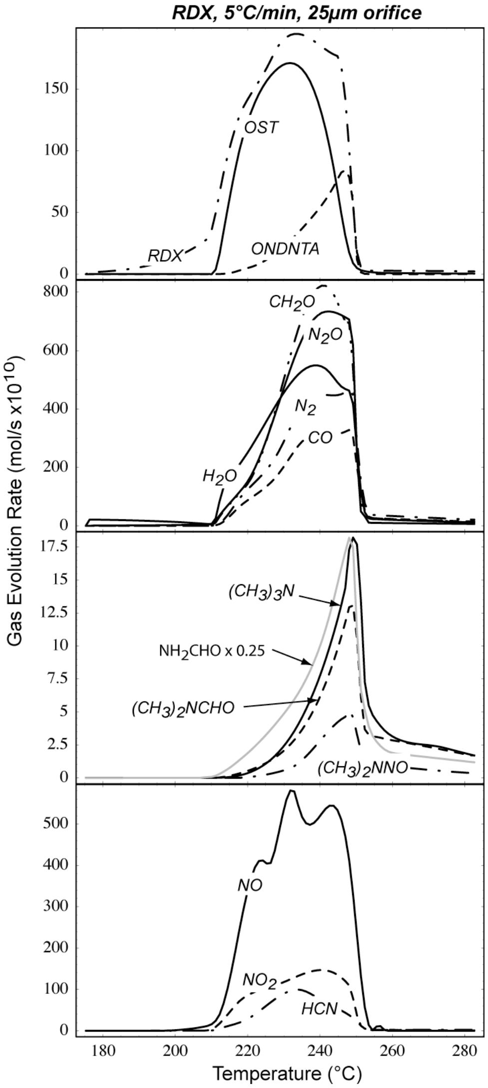


Figure 1. Gas evolution rates of products formed during the thermal decomposition of RDX.

<u>RDX Decomposition Model</u>. The data from a series of experiments probing the decomposition of RDX below and above its melting point have been used to construct a reaction scheme characterizing the main features of its decomposition process (Fig. 2). Mathematical models of this reaction scheme have been presented previously.[11] The reaction scheme is composed of reactions that occur in four separate phases that are present during the thermal decomposition experiments: solid phase, liquid phase, gas phase and a separate phase of the NVR. The reactions in the solid phase are limited to sublimation and melting of RDX. Note that

reactions occur on the surface of RDX particles as products from the decomposition of RDX, formed in the gas phase, deposit on the surface of the particles. Reactions in the gas phase occur in RDX that has evaporated from solid or liquid RDX. At temperatures above the melting point of RDX, reactions in liquid phase RDX will dominate the reaction process, since most of the RDX is present in the liquid phase during the course of an experiment. It is also important to note the role of NO and NO_2 in coupling several different reaction pathways in the overall reaction scheme.

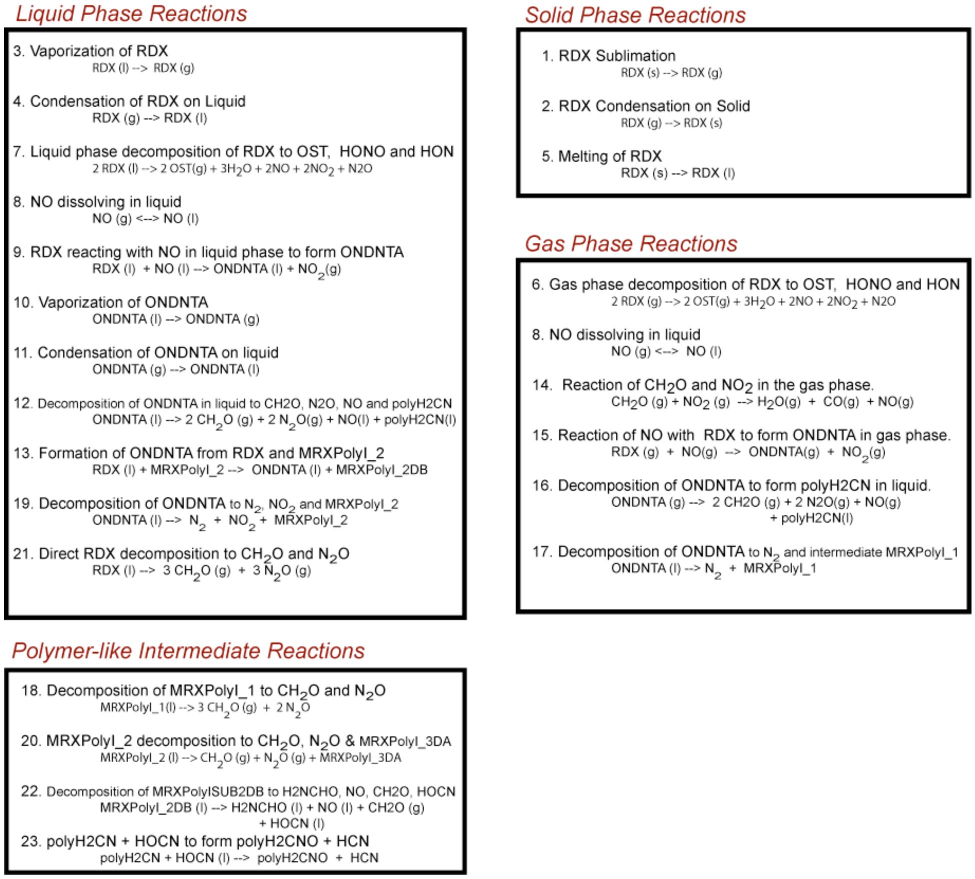


Figure 2. Reaction scheme characterizing the thermal decomposition of RDX above its melting point.

Burn Rate Modification. In order for a compound to be an effective burn rate modifier of an RDX-based propellant, it must either (1) react with RDX and effectively compete with the reactions that control the decomposition of RDX by itself, or (2) it must form gaseous products that interact and alter the combustion of the flame above the propellant surface. The first type of interaction will alter the pyrolysis processes on the surface of the burning propellant. The second type of interaction will alter the flame properties and affect the heat transfer to the propellant surface.

To most effectively alter the burn rate of RDX, a burn rate modifier should affect the first stages of the RDX decomposition process. As suggested by the reaction scheme shown in Fig. 2, a burn rate modifier may affect reactions at different steps in the RDX decomposition scheme.

The decomposition of TAGzT is currently being probed using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and Fourier Transform ion cyclotron resonance (FTICR) mass spectrometry methods. To date we have identified the products formed during its decomposition and developed a reaction scheme based on their identities and temporal behavior of their evolution during the course of an experiment.[12] The current reaction scheme is shown in Figure 3.

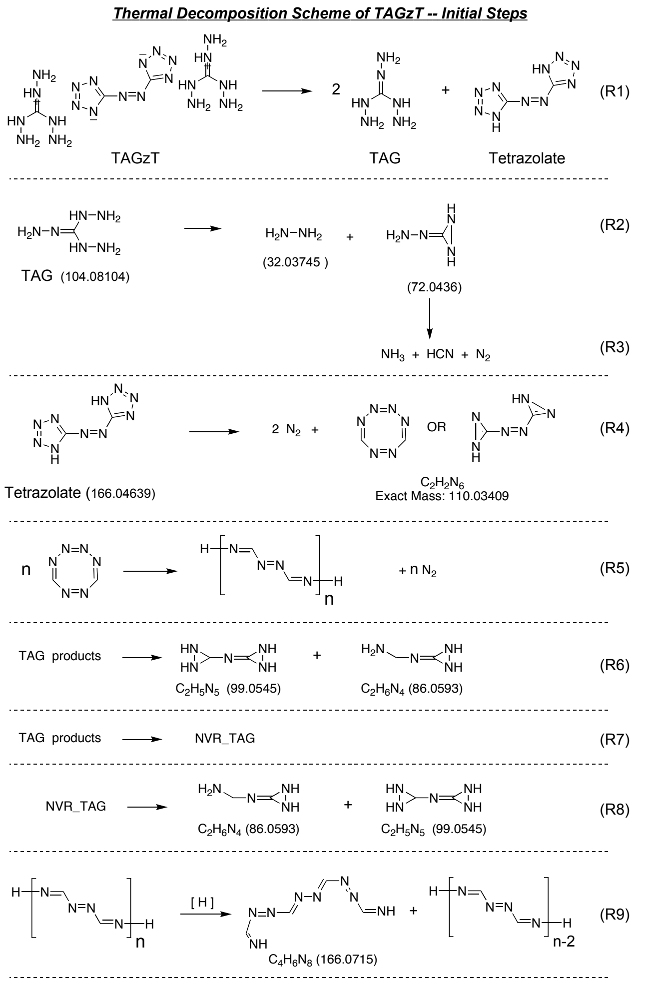


Figure 3. Reaction scheme characterizing the decomposition of TAGzT.

The first step involves the transfer of hydrogen from the triaminoguanidinium (TAG) cation to the azotetrazolate (AT) anion resulting In the formation of TAG and AT (R1). The TAG then decomposes to form hydrazine, N_2H_4, and an intermediate (R2) that may either decompose to lower molecular weight products (R3), HCN, N_2 and NH_3, or form higher molecular weight products, which may be volatile (R6) or (R7). The azotetrazolate decomposes releasing two N_2 molecules and forms a product with a molecular weight of 110, which may have a structure shown in R4. Higher confinement of the decomposition products promotes secondary reactions between the intermediate formed in the decomposition of TAGzT, which results in ~40wt% of the sample remaining as relatively non-volatile products after the TAGzT has decomposed. Further heating of this residue releases higher molecular weight gaseous products shown in Reactions R8 and R9.

Thus, there are two main features of the TAGzT decomposition process that may provide for interactions with RDX: (1) reaction with one or more of the gaseous products, NH_3, HCN, or N_2H_4, or (2) interaction of RDX with the non-volatile product. Hydrazine is the most reactive species formed in the decomposition of TAGzT.

The objective of the work presented in this paper is to determine the nature of the interactions that occur, if any, between TAGzT and RDX. The results from our experiments showing how TAGzT interacts with RDX are presented in this paper. In the future quantified data of the decomposition process will be acquired and mathematical models will be developed to represent the reaction kinetics of the decomposition process.

RESULTS AND DISCUSSION

EXPERIMENTAL METHODS

Instruments. Mass spectrometry is used to identify the compounds formed during the decomposition of mixtures of TAGzT and RDX. Simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) methods are used to measure the time and temperature dependence of the evolution of the decomposition products during the course of an experiment. The variables in an experiment (i.e., temperature, heating rate, pressure of the confined gaseous decomposition, extent of mixing of the compounds in the mixture) are altered in a controlled manner to provide data that can be used to elucidate the details of the reaction scheme. In this paper the formulas and temporal behaviors of the ions signals formed during the course of the decomposition experiments are used to develop our understanding of the interactions that occur between TAGzT and RDX.

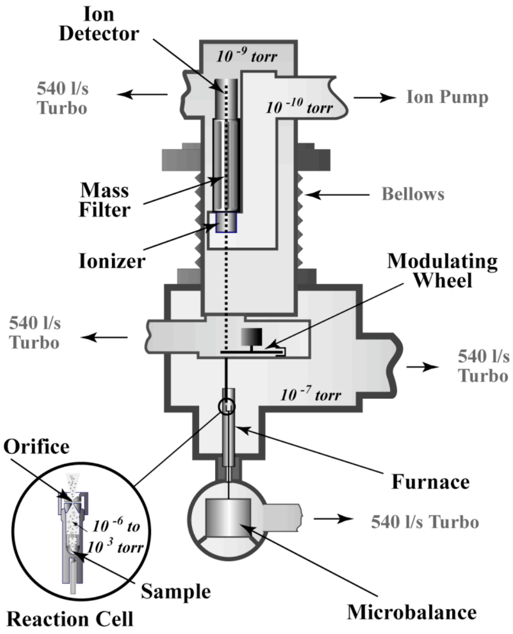


Figure 4. Schematic diagram of the STMBMS instrument.

The design and operation of the STMBMS instrument and details of the methods used to analyze the data have been descibed previously.[13-16] A schematic diagram of the instrument is shown in Figure 4. In a typical experiment a ~1 to 5 mg sample is placed in the reaction cell, which is then placed in the STMBMS instrument. The reaction cell is heated radiatively by the furnace. As the temperature of the sample in the cell rises, vapors from the sample fill the reaction cell. The vapor then exits through an orifice located in the top of the reaction cell. The mass loss of the vapor exiting the cell is recorded with the microbalance. The vapor exiting the cell is formed into a molecular beam, which is then modulated and the molecules in the modulated beam are detected with a quadrupole mass spectrometer. Analysis of the data allows the concentration of each gaseous product within the reaction cell to be determined as a function of time during the course of an experiment. Since the aim of this paper is to determine how TAGzT may interact with RDX, effort has not been expended to quantify the data at this time. Ion signals formed in the mass spectrometer from the various gaseous products that evolve from the reaction cell are presented. Note that some of the ion signals may arise from multiple sources (i.e., different decomposition products).

Since the quadrupole mass spectrometer that is used in the STMBMS instrument has limited resolution ($m/\Delta m \sim 200$ to 1000) and can measure only nominal mass values (i.e., integer values of atomic mass), it is difficult to determine the formulas of the ion signals found at the various m/z values in the data. To circumvent this problem, we also conduct thermal decomposition experiments using a Bruker Daltonics Apex II Fourier Transform ion cyclotron resonance (FTICR) mass spectrometer to measure the decomposition products. The FTICR mass spectrometer has a mass resolution greater than 100,000 and a mass accuracy of < 1.0 ppm. This allows the formulas of the ions formed in the mass spectrometer to be determined and the presence of ions with different formulas that occur at the same nominal m/z value to be identified (e.g., $CO^+ = 27.99437$ and $N_2^+ = 28.00560$). To collect mass spectra of the gases that evolve during the decomposition of TAGzT and RDX, approximately 1mg of the mixture is placed in a glass capillary tube and inserted into the instrument using a direct insertion probe (DIP). The DIP is heated in a controlled manner from room temperature to ~300°C and mass spectra are recorded as the sample is heated.

Materials. TAGzT and RDX are used in these experiments. The TAGzT used for these experiments were synthesized by the by Naval Surface Warfare Center at Indian Head (NSWC IHD). The material is a bright yellow, needlelike crystalline solid and is made by reacting triaminoguanidine hydrochloride (TAG-HCl) with sodium azotetrazolate (NaZT) and has an average particle size of about 200μm. Elemental analyses show the TAGzT is 98% pure. The

RDX was procured from Holston Defense Plant. The mean particle diameter of RDX is 5µm. It contains approximately 8.0 wt% HMX.

Sample preparation. The mixtures of TAGzT and RDX used in the experiment were prepared by mixing approximately 3 mg of RDX with 0.8mg of TAGzT. The powders were placed in the reaction cell and then mixed with a spatula. The reaction cells are fabricated from aluminum oxide. They are cleaned between each experiment by heating the reaction cell parts in air at 800°C for at least three hours. The reaction cells are kept in a desiccator prior to use. After the sample is loaded into the reaction cell, it is fitted with a cap that contains an orifice of a desired size for an experiment. For orifice diameters > 50 µm a cap fabricated from alumina is used. For orifice diameters ≤ 50 µm an orifice of the desired size located in a gold foil (25 µm thickness) is used. For experiments using an orifice in gold foil, the reaction cells are leak checked, using a He leak detector, prior to use in each experiment.

RESULTS

To illustrate the interactions that occur between RDX and TAGzT, the results from three decomposition experiments are presented: (1) TAGzT, (2) RDX, and (3) a TAGzT/RDX mixture. A ~25 µm diameter orifice and a heating rate of 2.5°C/min were used in each experiment.

Mass loss data. Comparison of the mass loss data from each experiment (Fig. 5) shows that there is an interaction between RDX and TAGzT. The TAGzT is characterized by a rapid weight loss commencing at ~190°C, followed by a more gradual weight loss proceeding from ~200 to 250°C. As described in the previous paper on TAGzT decomposition,[12] under the confinement conditions using a ~25µm diameter orifice about 60% of the TAGzT decomposes to volatile gases, NH_3, HCN, N_2, N_2H_4 and a product from the AT portion of TAGzT. The remaining 40% forms a nonvolatile product that subsequently decomposes as it is heated to higher temperatures. (Note: The apparent gain in mass observed in the experiments with TAGzT and TAGzT/RDX is due to the fact that the microbalance measures a force that has two components. One is the mass of the sample. The other is the thrust term due to the presence of the orifice and gases confined within the reaction cell. When gases are produced rapidly from material within the reaction cell, the thrust term becomes significant and forces the cell in a downward direction. The multiple peaks in the TAGzT data are most likely due to the formation of gas within the reaction cell and temporary blockage of the orifice.)

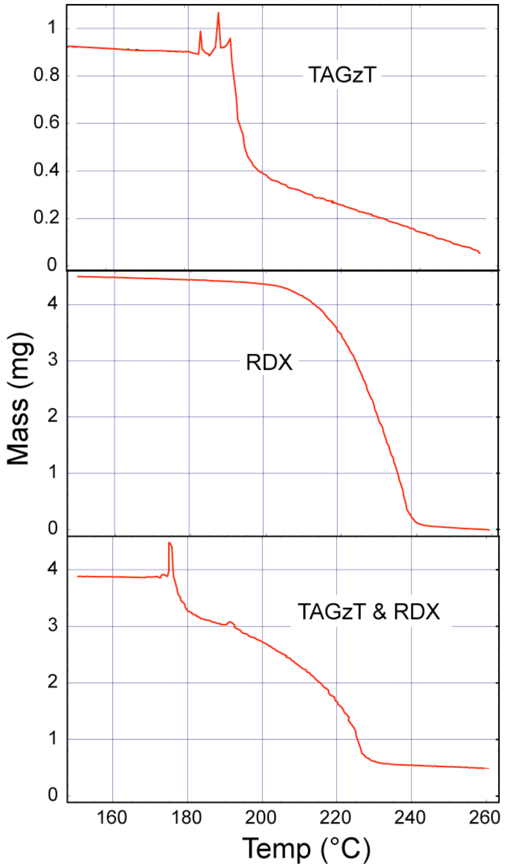


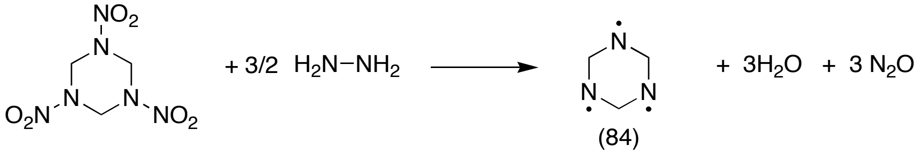
Figure 5. Mass loss data from experiments with TAGzT, RDX and a mixture of TAGzT and RDX.

RDX usually starts to decompose when it melts at ~200°C. However, since we are using a Holston grade RDX in these experiments, HMX dissolved in the RDX particles creates a lower melting eutectic mixture. The properties of the eutectic mixture control the rate of liquefaction of the sample, which in turn controls the rate of decomposition of RDX. Thus, the onset of RDX decomposition will start at a lower temperature and be more gradual when less pure Holston grade RDX is used.[7]

Comparison of the mass loss from the mixture of TAGzT and RDX with the mass loss from TAGzT and RDX individually shows: (1) The rapid mass loss, observed in the decomposition of TAGzT, commences at a temperature that is approximately 15°C lower in the mixture. (2) The mass loss attributable to the decomposition of RDX also starts at a lower temperature. (3) Some form of non-volatile residue that does not decompose significantly at temperatures up to 260°C may be formed. Thus, the mass loss data indicates that there is significant interaction between TAGzT and RDX. Examination of the temporal behavior of the decomposition products formed during the process provides further insight into the reactions that control the interaction of these two compounds.

Identities and rates of evolution of reaction products. The ion signals formed in the STMBMS mass spectrometer from the products that evolve from the reaction cell during the decomposition of TAGzT, RDX and a mixture of TAGzT and RDX provide the data that is used to determine how TAGzT interacts with RDX. The data comparing ion signals representing the temporal behaviors of various products are shown in Figures 6 and 7.

The data shows that there is a very strong interaction between hydrazine formed via reactions R1 and R2 in the decomposition of TAGzT and RDX as characterized by the following global reaction



(R10)

in which the hydrazine extracts NO_2 from the RDX and forms H_2O and N_2O. Close examination of the signals representing N_2H_4, H_2O, N_2O and a product represented by m/z=84 show the following: (1) The ion signal representing hydrazine, N_2H_4, drops from ~80 to ~2 c/ms. (2) As the TAGzT decomposes, which is characterized by the ion signal at m/z=110, the ion signals representing water, N_2O and 84 are much higher than during the decomposition of RDX by itself. (3) The rapid rate of H_2O and N_2O evolution diminishes after the TAGzT is consumed in the decomposition process. (4) These reactions occur prior to the onset of the main decomposition process of RDX, characterized by the evolution of oxy-s-triazine (OST, 97) and hexahydro-1-nitroso-3,5-dinitro-s-triazine (ONDNTA). *These features demonstrate that hydrazine, formed in the decomposition of TAGzT, interacts strongly and rapidly with RDX prior to onset of the main RDX decomposition processes*.

Two of the other gaseous products formed during the decomposition of TAGzT, HCN and N_2, do not appear to interact strongly with RDX or its decomposition products. Comparing the data from TAGzT with the data from the mixture of TAGzT and RDX shows that the ion signals representing HCN and N_2 do not change to a significant extent.

There appears to be more ammonia, NH_3, formed during the decomposition of the mixture of TAGzT with RDX than in TAGzT by itself. The peak of the NH_3^+ signal in the experiment with TAGzT/RDX is about 85 c/ms compared to about 16 c/ms in the experiment with TAGzT by itself. After accounting for the slightly higher ion formation probability in the mass spectrometer in the experiment with TAGzT/RDX, the higher value suggests that more ammonia is formed from the mixture of TAGzT and RDX than from TAGzT alone. This may be due to the interaction of the hydrazine with the RDX, or possibly presence of elementary reactions other than those that comprise the global reaction R10.

The main product formed from the azotetrazolate portion of the TAGzT molecule ($C_2H_2N_6$, m/z= 110, 82) appears to evolve at a greater rate in the experiment with the mixture of TAGzT and RDX than in TAGzT alone. This suggests that less non-volatile polymeric product (NVPP) may be formed via reaction R5. This is also consistent with the fact that the ion signal from the product (m/z=166) formed from the dissociation of the NVPP via reaction R9 is not observed in the experiment with the mixture of TAGzT and RDX.

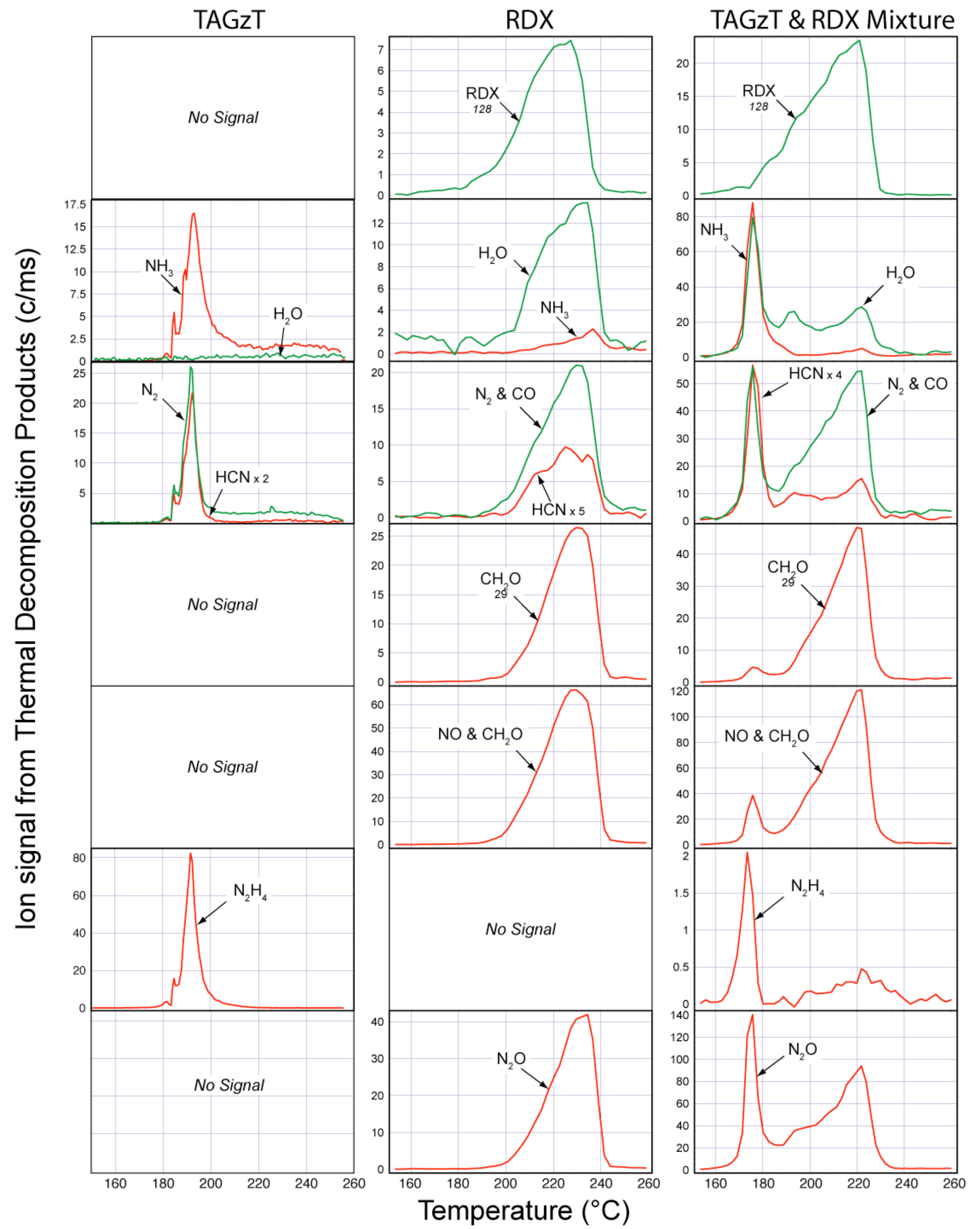


Figure 6. Ion signals formed in the mass spectrometer of the STMBMS instrument from products that evolve from the reaction cell during the decomposition of TAGzT, RDX, and a mixture of TAGzT and RDX. The data was collected in the same experiments for which the mass loss data is shown in Fig. 5. Ion signals representing higher molecular weight products are shown in Fig. 7. (Note: the efficiency for creating ions at a specific m/z value from a gaseous product varies from experiment to experiment. For example, the efficiency of forming ions in the experiment with a mixture of TAGzT and RDX is ~50% higher than in the experiment with RDX.)

Although there is a strong interaction between hydrazine and RDX, the main features

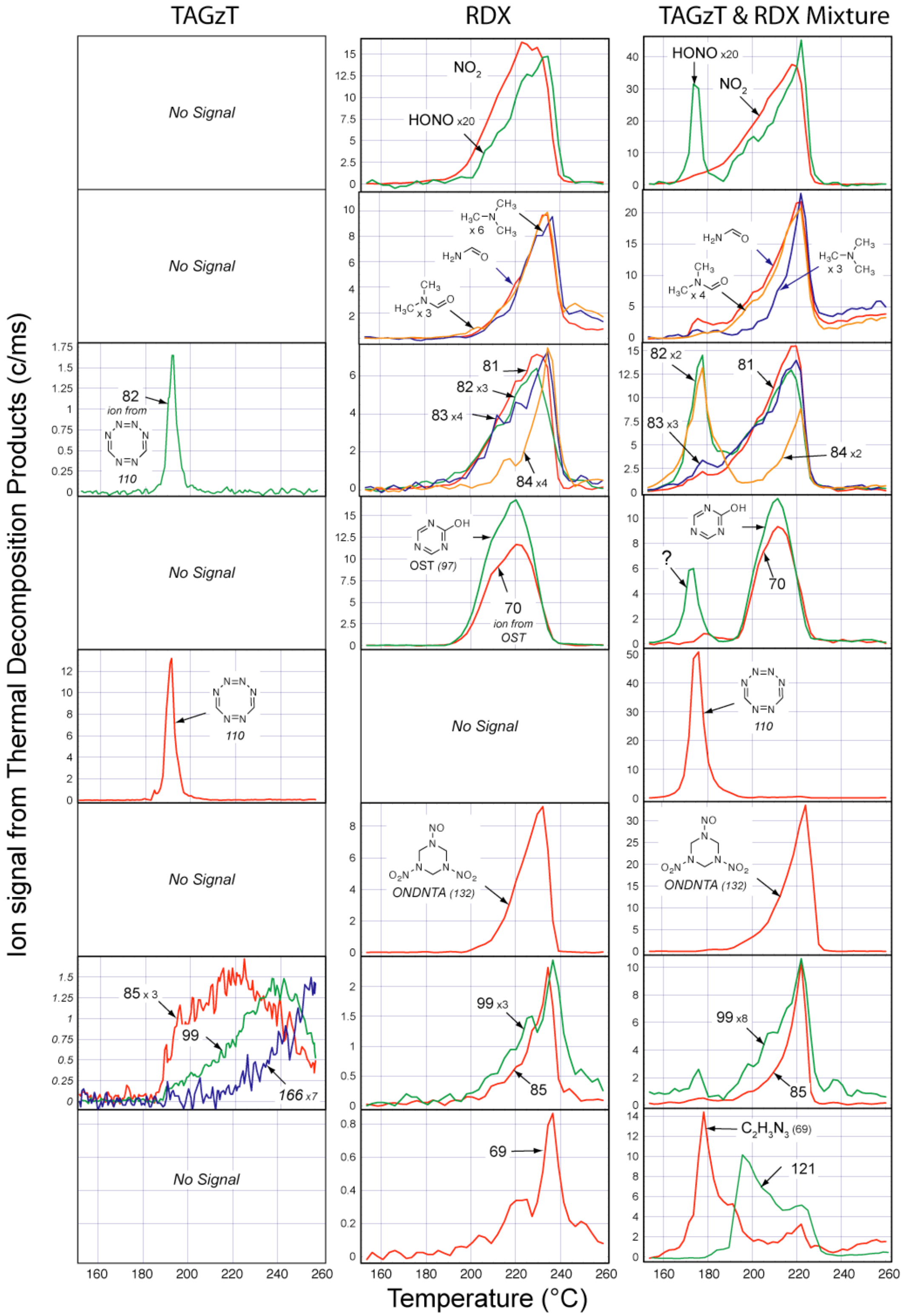


Figure 7. Ion signals formed in the mass spectrometer of the STMBMS instrument from products that evolve from the reaction cell during the decomposition of TAGzT, RDX, and a mixture of TAGzT and RDX. The data was collected in the same experiments for which the mass loss data is shown in Fig. 5. Ion signals representing lower molecular weight products are shown in Fig. 6.

characterizing the decomposition of RDX, after there has been an interaction with hydrazine, are quite similar to RDX by itself. The primary reactions that control the decomposition of RDX are reactions 7, 9 and 12, which are listed in Fig. 2. These reactions are characterized by the ion signals for OST (m/z= 97 & 70), ONDNTA (m/z=132), and the main gaseous decomposition products, H_2O, N_2/CO, CH_2O, and N_2O, which are shown in Figures 6 and 7.

The OST tracks the direct decomposition of RDX in the liquid phase. Comparison of the OST signals from the experiment with pure RDX to those from the experiment with the TAGzT/RDX mixture show similar behavior. The evolution of OST starts at ~192°C and it climbs gradually as the eutectic mixture of RDX and HMX in the RDX particles gradually melts. The ion signals formed from OST are at m/z values of 97 and 70 and usually have a ratio of ~ 1.5:1, as is observed during the initial portion of the RDX decomposition process. The increase in the signal at m/z=70 relative to the signal at m/z-=97 originates from the formation of an additional product during the later stages of the RDX decomposition process as described previously.[10] This occurs in both the RDX and TAGzT/RDX experiments.

The formation of ONDNTA occurs through the reaction of RDX with NO (reaction 9 in Fig. 2) and is similar for experiments with RDX and TAGzT/RDX. However, closer examination shows that the evolution of ONDNTA starts at a slightly lower temperature in the mixture of TAGzT and RDX than it does in RDX alone (~192°C vs. ~198°C). This is also supported by the earlier appearance of signals representing the decomposition products from ONDNTA (e.g., CH_2O and N_2O, reaction 12 in Fig. 2) in the mixture of TAGzT and RDX than in RDX alone.

Products formed during the later stages of the decomposition of RDX appear to be relatively unaffected by the TAGzT. For example the signals representing formamide, N,N-dimethylformamide, and trimethylamine (Fig. 7) are quite similar in the experiments with RDX and the mixture of RDX and TAGzT.

Based on these observations of the similarities and differences in the evolution of products from experiments with TAGzT, RDX, and a mixture of TAGzT and RDX, we draw the following conclusions regarding the nature of the interaction of TAGzT and RDX:

1. Hydrazine, formed in the decomposition of TAGzT, interacts directly with RDX.
2. The hydrazine reacts with RDX by abstracting the NO_2 groups, forming water and N_2O as the main products of the reaction.
3. The decomposition of TAGzT, and resulting generation of hydrazine, occurs before the RDX melts <u>in our experiments</u>. Thus, the reaction of hydrazine and RDX must occur in the gas phase and on the surface of the RDX particles.
4. After the available hydrazine is consumed, the RDX melts and undergoes decomposition in a manner that is similar to RDX by itself.
5. The reaction on the surface of RDX particles is accelerated and is most likely due to the previous interaction of RDX on the surface with hydrazine. However, it is also possible that the NVPP formed in the decomposition of TAGzT may affect the early stages of the RDX decomposition. The products formed in the affected region on the surface are those typically associated with the decomposition of RDX via the ONDNTA reaction intermediate.

Thus, the new dominant interaction is a very strong reaction between hydrazine and RDX.

The interaction of the TAGzT with RDX is somewhat more complex than the simple reaction scheme that has been outlined. Further examination of the data in Figures 6 and 7 shows signals at several other m/z values that are indicative of interactions between the TAGzT decomposition products and RDX. These signals are associated with NO, HONO, $C_2H_3N_3$ (69), and unidentified products at m/z values of 97 and 121. The signals representing NO and HONO would appear to be minor products formed in the interaction of hydrazine with RDX. This would be expected. The signal at m/z=97 is not OST since there is not a corresponding signal in the mass spectral data at m/z=70. The signal at m/z=121 appears after the TAGzT has decomposed and during the early phase of the RDX decomposition. This suggests that it is associated with a product formed on the surface of the RDX particles during the interaction with TAGzT. More careful FTICR mass spectrometry measurements will be made to identify these currently unknown products.

Finally, it should be noted that the TAGzT decomposes at a temperature that is 15 to 20°C lower when it is in the presence of RDX than when it is by itself. This suggests that RDX is transported to the surface of the TAGzT particles, reacts on the surface of TAGzT, and results in the onset of decomposition of TAGzT at a lower temperature.

BURN RATE MODIFIERS FOR NITRAMINE PROPELLANTS

While burn rate modifiers for *double-base* propellants have been available for many decades, the development of burn rate modifiers for *nitramine-based* composite propellants had been an elusive quest.[5] Various lead salts have been shown to catalyze the reactions of the nitrate esters used to fabricate double-base propellants. But until recently, there has been little success in finding compounds that will alter the reaction process of the nitramine ingredients, RDX or HMX. Normally, the decomposition of RDX and HMX is controlled by their own self-contained reaction processes. However, advances over the past several years in the synthesis of high nitrogen energetic ingredients has provided a means to increase the burning rates of RDX propellants. These materials, which include TAGzT, have been used successfully as burning rate modifiers for RDX propellants by the Department of Defense.[1] Why some high nitrogen compounds modify the burn rate of RDX-based propellants, while others do not, has been an unresolved question.

TAGzT & RDX Propellant

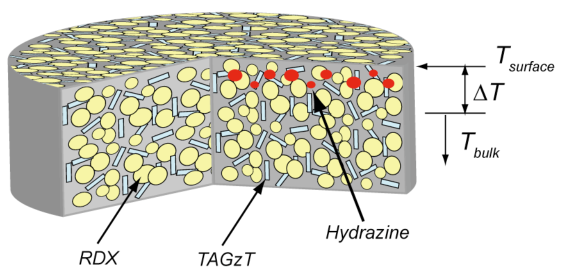


Figure 8. Illustration of hydrazine formed in the decomposition of TAGzT acting as a burn rate modifier in nitramine composite propellant. Relative sizes of RDX and TAGzT are illustrative. Previously measured burn rates used needle shaped TAGzT (~20μm w x ~ 100 μm l) and 5μm RDX powders.[1]

The results of our current experiments with TAGzT and RDX show that the hydrazine formed in the decomposition of TAGzT will react with RDX faster than RDX can decompose on its own. Thus, the ability to create hydrazine within a nitramine-based propellant, provides a reaction pathway that can be adjusted to control the rate of reaction of RDX. This is a key feature that should allow propellants to be designed to have desired burning rate characteristics.

A conceptual design for a burn rate modified nitramine-based propellant is shown in Figure 8. The temperature gradient established below the surface of the burning propellant (temperature: $T_{surface} > T_{bulk}$) can be used to control the interaction between the hydrazine formed in the decomposition of TAGzT and the RDX. In this case, since the TAGzT decomposes at a lower temperature than RDX, the hydrazine should be generated at a depth further from the surface of the burning propellant than the RDX. Thus, the hydrazine should flow up through the RDX particles. In a steep temperature gradient, the RDX will melt and the hydrazine should flow through a melted layer of RDX.

The fact that hydrazine reacts rapidly with RDX compared to the decomposition of RDX itself opens a wide range of methods that could be employed to tailor the burn rate of RDX-based propellants. Several possible approaches include:

1. Adjustment of the particle sizes and particle size distributions of RDX and the hydrazine-generating compound (e.g., TAGzT) to obtain an appropriate balance between the rate of formation of hydrazine and the rate of decomposition of RDX by itself.
2. Incorporation of other ingredients in the propellant binder that would moderate the generation of hydrazine in the pressure range that is required to create a plateau burning propellant.
3. Synthesis of other compounds that generate hydrazine at various rates over a wide range of temperatures. These would enhance the ability to tailor the burn rates by providing a broader selection of ingredients.
4. The use of HMX instead of RDX if a larger temperature difference is required between the hydrazine generating compound (e.g., TAGzT) and the energetic nitramine.
5. Utilization of other nitramines in conjunction with RDX or HMX to effectively tailor the interaction with TAGzT. For example, 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K6) has a lower melting point (~180°C) and decomposes more rapidly than RDX.[17]

These are a few examples of how compounds that generate hydrazine could be used to advantage to modify the burn rate behavior of propellants.

SUMMARY AND CONCLUSIONS

STMBMS experiments with mixtures of TAGzT and RDX provide insight into the decomposition of the individual ingredients, as well as the interactions between the two compounds and their decomposition products. This information provides insight into reactions that are likely to play an important role in the initial steps in the combustion of TAGzT/RDX-based propellants.

The two compounds decompose over the same temperature range of 170 to 250°C which allows reactions between the each compound and their decomposition products to occur.

TAGzT decomposes via a relatively complex multistep nonlinear reaction process, which has been described in another paper presented at this meeting.[12] However, for considering its interaction with RDX the components of this complex process may be divided into two branches: (1) the formation of volatile gaseous products, NH_3, HCN, N_2 and N_2H_4 and (2) the formation of non-volatile products that remain in the condensed phase of the sample and decompose at higher temperatures. Thus, the decomposition of RDX may be altered by TAGzT in two ways: (1) the gaseous products may interact with RDX in the gas phase or may diffuse into the RDX and react with RDX within the condensed phase, or (2) the RDX may be transported to the non-volatile TAGzT product and react.

The dominant interaction occurs between RDX and N_2H_4. This reaction is very rapid and results in the formation of H_2O, N_2O and various forms of remnants from the RDX ring. The amount of N_2H_4 that evolves from the reaction cell during the course of an experiment is approximately a factor of 100 lower when RDX is present in the reaction cell compared to when it is not present. By comparison, NH_3 does not react appreciably with RDX under similar conditions.

The products that evolve due to the interaction of N_2H_4 with RDX indicate that the reaction involves reaction with the NO_2 groups on RDX. The fact that products that are associated with the decomposition of the RDX ring, HCN and CH_2O, are not observed to an appreciable extent suggests that removal of one NO_2 group from an RDX molecule does not trigger a rapid decomposition of the remaining intermediate. The data indicates that hydrazine removes all three nitro groups from an RDX molecule.

TAGzT can effectively alter the decomposition process of RDX. This occurs primarily via the formation of N_2H_4 in the decomposition of TAGzT and its subsequent rapid interaction with RDX.

Thus, this explains why TAGzT is a good burn rate modifier. The key feature is the formation of hydrazine during the decomposition process. Since formulating a propellant will involve developing a composite material that includes powders of RDX and TAGzT, it should be possible tailor the burn rate of a TAGzT/RDX-based propellant by controlling the transport of N_2H_4 between ingredients in the propellant. For example, mixtures of very fine powders may have a higher degree of burn rate enhancement than mixtures of larger particles.

Finally, the key feature of TAGzT that enables its interaction with RDX is the formation of hydrazine during its decomposition. Thus, other compounds that form hydrazine during their thermal decomposition may also be good candidates for burn rate modifiers.

FUTURE WORK

Results from our initial experiments on the decomposition of TAGzT and RDX mixtures have been presented. To build on this effort further work is planned in the following areas: (1) Deuterium and ^{15}N-labeled RDX will be used to elucidate the mechanism of reaction between N_2H_4 and the NO_2 groups on RDX. (2) Further refinement of the reaction mechanism to describe the interaction of TAGzT with RDX. (3) Investigation of the reaction of TAGzT with other types of nitramines and the ingredients used in propellant binders. (4) Development of mathematical models to describe the reaction processes that control the decomposition of RDX, TAGzT and their interaction. (5) The examination of TAGzT/RDX-based propellants.

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