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REACTIONS OF TAG-BASED ENERGETIC MATERIALS

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ABSTRACT

A new paradigm, “Concepts, Methods and Protocols for Reaction Hierarchy and Network Development” (CoMPReHND) is under development and has been applied to investigate the thermal decomposition of TAG-based salts and their interaction with RDX over a range of conditions that are relevant to performance, safety, and long-term aging behavior of gun propellants. Four TAG-based salts have been examined to investigate the role of the anion in the reaction network. The four salts include: TAGzT, TAG-TATTz, TAG nitrate, and TAG chloride. The reaction network of TAG-TATTz and TAGN have features similar to those found in our previous studies of TAGzT. The relative fraction of hydrazine observed from the four salts when examined by themselves has the following sequence: TAGzT>TAG-TATTz>TAGN>TAGCl, indicating that the smaller inorganic anions, Cl^- and NO_3^-, are more reactive than the organic anions. Reactions of TAGzT, TAG-TATTz, and TAGN with RDX show that the extent of reaction of hydrazine with RDX is comparable for each salt. This suggests that even though the inorganic anions react more readily with hydrazine than the organic anions, the rate of reaction of hydrazine with RDX is faster than its rate of interaction with the anions. This effectively overcomes the differences in the reaction rate of hydrazine with the different anions. The results also indicate the reaction of hydrazine with RDX occurs primarily in the gas phase. Experiments investigating the onset of decomposition of TAGzT, TAG-TATTz and TAGN show that the initial reaction for each salt is dissociation to TAG and an associated product from the anion. The observed onset temperature for decomposition is between 110 and 120°C for TAGzT and TAGN and 165°C for TAG-TATTz.

INTRODUCTION

High nitrogen compounds are of interest for the development of advanced gun propellants. For example, it has been shown that replacing ingredients such as RDX with triaminoguanidinium nitrate (TAGN) or triaminoguanidinium azobitetrazolate (TAGzT) in gun propellants increases their burn rate.[1, 2] In addition, the high nitrogen content of the expanding gaseous products of propellants formulated with these ingredients will reduce gun barrel erosion and increase the service life of guns.

To introduce new ingredients into gun formulations requires addressing standard life cycle issues: (1) the ability to manufacture the new formulation safely; (2) the ability of the new formulation to meet safety and insensitive munition (IM) requirements; and (3) the long-term stability of the material during deployment and storage. The reactivity of the new ingredients and their interactions with other ingredients in the formulation underlies the ability to successfully develop a new propellant that will meet these standard life cycle requirements.

To address life cycle issues for new formulations, the conventional development paradigm utilizes a synthesize-and-test approach. A new compound is synthesized, usually based on target goals based on performance (i.e., higher energy content, larger fraction of

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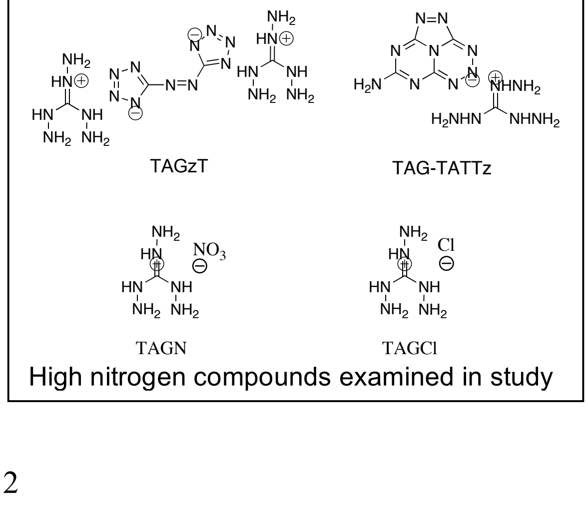
nitrogen). If it meets the expected performance requirements, is thermally stable, and has acceptable impact sensitivity, the synthesis process is scaled up to create enough material for testing. With sufficient material available, tests to measure performance, such as burn rate for a propellant, and safety characteristics, such as shock sensitivity, and IM characteristics are conducted. The results from these are often in the form of go/no-go information and provide limited information. Thus, the amount of insight that can be gained on how to design the next molecule to meet the performance and life cycle requirements is limited. Furthermore, it is costly and time consuming to do the scale up and conduct the required tests.

To overcome these limitations, we are developing a more scientific approach for evaluating new ingredients. In this approach, we first recognize that the reaction behavior of a propellant or explosive formulation, over the many different environments encountered during its life cycle, is determined by a network of reactions and reaction processes. How a material behaves will depend on which parts of the reaction network play a dominant role in the reaction process for the set of conditions that are defined by a particular reaction environment. For example, it is quite likely that the parts of the reaction network that are important for controlling the first steps in the combustion processes will be different from those that are important in the manufacturing process, which in turn are likely to be different from those that are important for long-term aging. Thus, the scientific approach requires determining and understanding the reaction network that characterizes a new ingredient and its interaction with other ingredients in a formulation.

To determine the network that controls the reaction processes of an energetic material is difficult and cannot be accomplished using commercially available instruments and methods. To develop a scientific approach has required: (1) Understanding and defining the concepts needed to characterize complex reaction mechanism of compounds in the condensed phase. (2) Devising instrumental methods and numerical algorithms to identify chemical species and measure their concentrations as a function of time during the course of an experiment. (3) Creating the protocols needed to design the experiments, analyze the data and interpret the results in order to determine and characterize the reaction network. The instruments and experimental methods have been described previously.[3] Currently, we are developing a manuscript[4] to describe how these methods are used to determine the networks that characterize these complex processes. The new paradigm we have created is known as "Concepts, Methods and Protocols for Reaction Hierarchy and Network Development" (CoMPReHND). All of the features of CoMPReHND have been developed through our extensive work over the years on RDX, HMX and other energetic compounds.

Examination of new HiN compounds and their interaction with other ingredients in gun propellants is our first application of CoMPReHND to determine the reaction networks of new formulations. This class of compounds was selected for investigation based on previous results that showed that some HiN compounds, such as TAGzT, increased the burn rate of nitramine-based gun propellants, whereas similar compounds such as guanidinium azobitetrazolate (GUzT) did not. The reason for this difference was unknown.

In our initial work, the decomposition of TAGzT and GUzT, and their interactions with RDX, was investigated. During the thermal decomposition of TAGzT large quantities of hydrazine are formed,[5] whereas this compound is not observed in the decomposition of GUzT.[6] In addition, in experiments with mixtures of TAGzT and RDX,[7] it was discovered that hydrazine formed from TAGzT interacts with, and leads to the decomposition of, RDX faster than RDX can react by itself. Thus, the generation of N_2H_4 from TAGzT and its interaction with RDX



High nitrogen compounds examined in study is a likely reason for the observed increase in burning rate of TAGzT modified propellant.[2]

Recent work on the development of gun propellant formulations containing TAGzT has raised concern regarding the thermal stability of TAGzT and its compatibility with other ingredients. This raised a number of questions that are addressed in this paper: (1) At what temperature does TAGzT first decompose? (2) What molecular properties determine the initial decomposition? (3) How does TAGzT, or its decomposition products, interact with other ingredients? (4) How can other TAG-based molecules be designed that are more stable than TAGzT, but will produce hydrazine in sufficient quantity to interact with RDX in the propellant?

To address these questions, we focus on the role that the anion may play in the decomposition process of TAG-based compounds. Since TAG-based compounds are salts, their stability may depend on the barrier that limits their transition from an ionic to neutral form. Once the neutral compounds are formed from the cation and anion, then the reaction network will depend on how each compound reacts individually and how they, and their decomposition products, interact with each other. For example, in our previous work it was observed that hydrazine, formed from TAGzT, reacted with RDX. This process requires that the N_2H_4 must persist for a length of time that is sufficient to encounter, and react with, an RDX molecule. If the anion formed in the initial decomposition process reacts rapidly with hydrazine, then transport of hydrazine from its point of origin at a TAGzT particle to the region where RDX is located will be limited. This would limit any enhanced rate of reaction of the RDX by hydrazine.

To examine these aspects of the reaction of TAG-based compounds, the reactions of four TAG salts have been investigated. They include TAGzT, triaminoguanidinium triazoloaminotriazinyltetrazine (TAG-TATTz),[8] TAGN, and TAG chloride (TAGCl). The experiments examine the initial decomposition reactions, the relative amount of hydrazine that evolves from each compound, and the effect of each compound on the reaction process of RDX.

METHODS

CoMPReHND has been used previously to determine the elements and linkages in the networks that control the thermal decomposition of TAGzT,[5] RDX[9, 10] and their interaction.[7] The instruments and methods used to conduct the thermal decomposition experiments are described elsewhere.[3, 11-13]

To investigate the role of the anion in the decomposition of TAG salts, we initially examine important

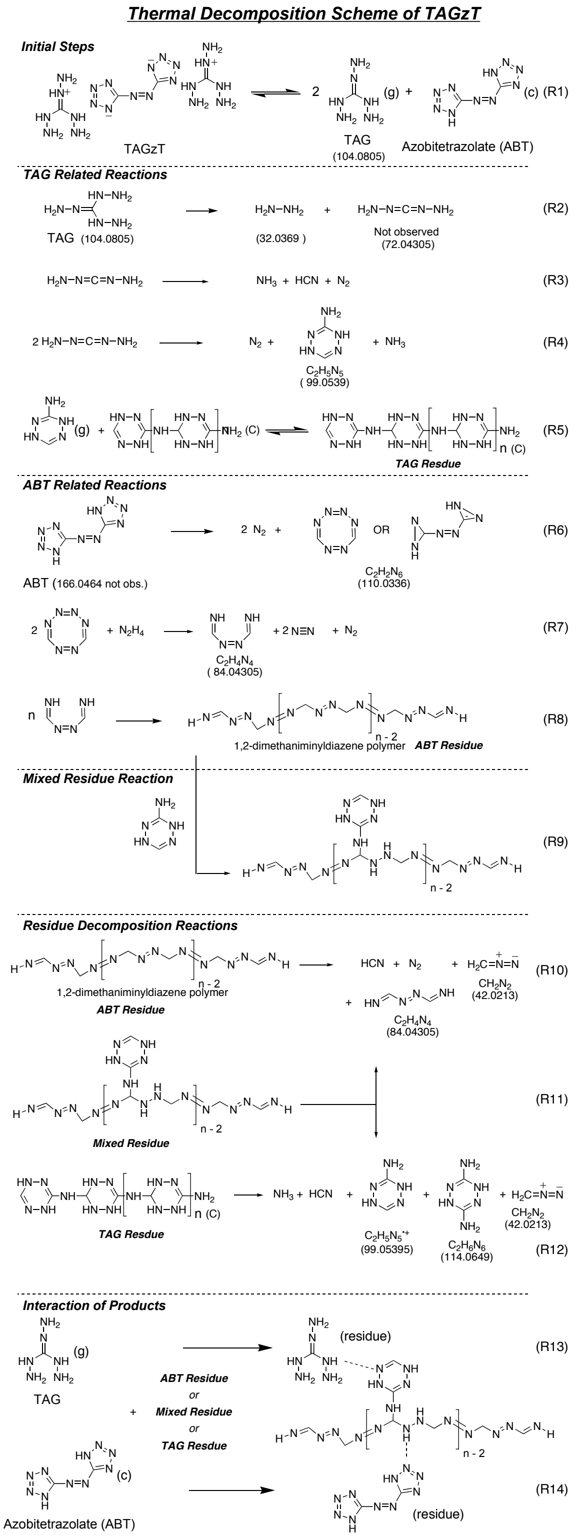


Figure 1. Reaction mechanism of TAGzT decomposition. Species listed with m/z values have been identified and their rates of formation measured in our experiments along with NH_3, HCN and N_2.

features in the reaction mechanism of TAGzT (Fig. 1).[5] The first step of the decomposition process involves the dissociative sublimation of TAGzT to TAG and azobitetrazolate (ABT) via R1. TAG is a volatile product while ABT is not. The TAG then decomposes into hydrazine (R2) and an intermediate that decomposes to NH_3, HCN and N_2 (R3). Diaminocarbodiimine is a known reactive intermediate, but it is not observed directly in our experiments. ABT decomposes to two moles of N_2 and $C_2H_2N_6$ (R6). The decomposition products from TAG and ABT may undergo further reaction to form compounds such as $C_2H_5N_5$ (99) or $C_2H_4N_4$ (84), via reactions R4 and R7, respectively. These compounds may in turn form less volatile, polymeric-like, compounds via reactions such as R8 and R9. These compounds may either decompose via reactions such as R10 through R12, or form a feedback loop and react with TAGzT via reactions such as R13 and R14 in an "autocatalytic-like" manner.

To design new high nitrogen ingredients, such as TAG salts, that will meet future munition 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. For the TAG salts the following steps may be considered critical:

1. <u>Performance</u>. Hydrazine formed from TAGzT has been shown to react more rapidly with RDX than RDX can decompose by itself.[7] Thus, compounds that decompose to form substantial amounts of hydrazine (via R2 for TAGzT) are likely to be good burn rate modifiers, if the hydrazine can survive 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 burn rate modifier.

2. <u>Manufacturability & long-term aging</u>. To be useful, compounds must be thermally stable. Compounds must be stable at the elevated temperatures often used in the manufacturing process. Thus, it is important to understand the initial steps of the decomposition process (R1) as well as processes that may have an "autocatalytic effect" (R13 and R14).

3. <u>Safety and IM behavior</u>. Compounds that form larger more stable molecules versus

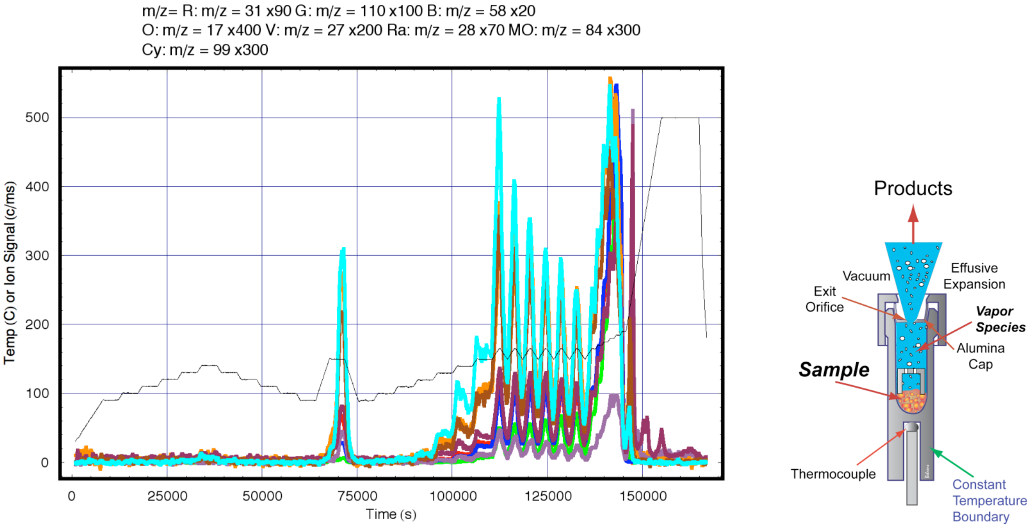


Figure 2. Illustration of experimental protocol used to examine the reaction processes in TAG based salts. Data from decomposition of TAGzT. Black curve indicates temperature profile for experiment. Other curves are ion signals, measured with a mass spectrometer, representing the various products shown in the TAGzT reaction scheme (Fig. 1). Color codes for m/z values and scaling factors are listed on top of graph. Data collected under low confinement, sample mass 2.49 mg. Cross section of reaction cell used in STMBMS experiments is shown on right. Confinement is altered by using exit orifices with various diameters (~50 to 1000μm).

smaller gaseous molecules when they decompose are likely to be safer and more likely to meet IM requirements. Thus, compounds that form intermediate products such as those shown in reactions R4, R5, R8, and R9 may result in safer munitions.

To screen new compounds we have developed a new experimental protocol using our simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) instrument that evaluates various aspects of important reactions (e.g. R1, R2, R6 and R13/R14) in one experiment. The protocol is illustrated in Figure 2 with data from the decomposition of 2.49mg of TAGzT under low confinement. The temperature of the sample is varied in a controlled manner over a temperature range from 20 to 500°C. The first set of heating/cooling steps is set to identify the first steps in the decomposition process and determine the onset temperature of decomposition. The next interval is a heat and hold section to determine if there is a delay time associated with the onset of secondary reactions. This provides insight into the complexity of the reaction process and whether the reaction network contains coupled reactions or feedback loops (often referred to as autocatalysis). The next set of temperature steps is to determine the onset of different secondary reactions in the network. This is followed by a series of heating/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 500°C to decompose any relatively non-volatile species that were formed during the decomposition process. This provides insight to 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 products are represented by the ion signals at the following m/z values: N_2H_4 (m/z = 31), $C_2H_2N_6$ from azobitetrazolate (ABT) (110), TAG (58, daughter ion), NH_3 (17), HCN (27), N_2 (28), $C_2H_4N_4$(84), and $C_2H_5N_5$(99).

The data in Fig. 3 illustrates how changing the extent of confinement of gaseous species within the reaction cell is used to control the reaction process and provide insight used to construct a reaction network to characterize the thermal decomposition of a compound. The three graphs in the left column of Fig. 3 compare ion signals representing the rate of formation of various species under low, high and medium confinement. Under low confinement (3a), the species evolve gradually over the course of the entire experiment. The rates of evolution of the various species rise and fall as the sample is heated and cooled during the cycling stage. This is followed by their increasing rate of evolution in the sequence of isothermal steps that follow the cycling stage. In contrast, the signals representing the same species when the experiment is conducted under high confinement (3b) is quite different. The more volatile products evolve only during the first two cycles of the cycling stage and the evolution of the species from the non-volatile residue falls through the remaining cycles. The rate that species evolve from the residue formed in the decomposition of TAGzT rises as the sample is heated to 500°C.

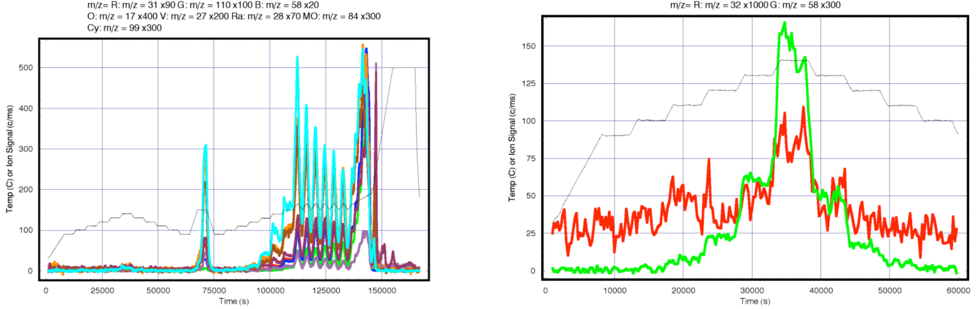
The complex behavior that controls the decomposition of TAGzT between the low and high confinement conditions can be investigated in more detail with an experiment run under medium confinement conditions as illustrated with the data in Fig. 3c and 3f. In this experiment, one observes the evolution of TAG (blue) in each stage of the experiment and an increasing rate of evolution of the thermal decomposition species during each subsequent heating/cooling cycle during the thermal cycling stage of the experiment. This shows that a portion of the reaction network for the decomposition of TAGzT consists of a feedback loop in which products formed earlier in the process accumulate and lead to an increasing rate of reaction as the experiment progresses. The rate of this feedback loop depends on the pressure of the confined gases. In our lower confinement case this feedback loop contributed only slightly to the overall reaction of the sample whereas in the higher confinement case it led to a much more rapid decomposition of the sample.

The protocol provides data to determine the reaction that initiates the decomposition of the compound of interest and to provide data to determine how fast this occurs as a function of temperature. The data illustrating this feature for TAGzT is shown in Fig. 3d. For TAGzT the initial reaction involves the reversible decomposition of TAGzT to TAG (green) and ABT (the reversibility was determined in experiments not presented here). The data collected at set of isothermal steps can be used to determine the parameters that determine the pressure of TAG formed from the dissociative sublimation of TAGzT. In our experiments the first decomposition of TAGzT is observed at ~110°C. It is also worthwhile to note that if the reaction conditions are altered in such a way that TAG decomposes, or reacts with another ingredient, then the reaction rate of TAGzT will increase to satisfy the equilibrium conditions.

Finally, the complex nature of the decomposition of TAGzT is further illustrated with the data in Fig. 3e. If the decomposition of TAG to N_2H_4, NH_3, HCN, and N_2 as summarized by reactions R2 and R3, then their rate of formation should be proportional to the concentration of TAG in the gas phase (characterized by green curve in Fig. 3e). This is not the case. There is a delay of approximately 2000 seconds from the time the TAG reaches a stable concentration in the reaction cell at 150°C and the time that the four gaseous species start to evolve from the sample. This suggests that some species is being formed in the condensed phase (most likely

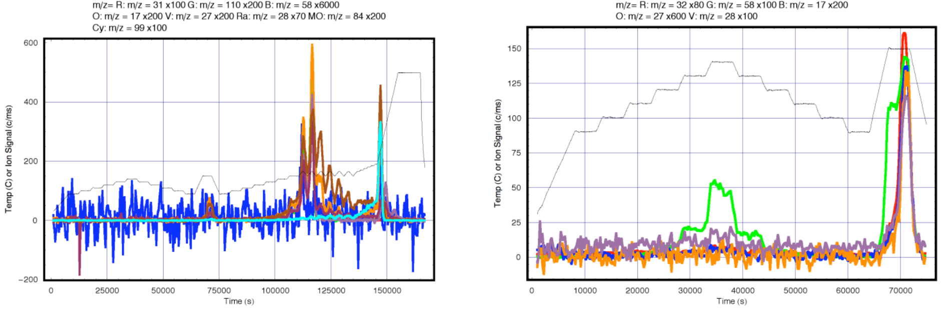
a. Low confinement (1000 μm) ; 2.49mg TAGzT

d. Low confinement; 2.49mg TAGztT



b. High confinement (~50μm), 2.24mg

e. Low confinement: 2.49mg



c. Medium confinement (~100μm); 2.22mg

f. Medium confinement; 2.22mg

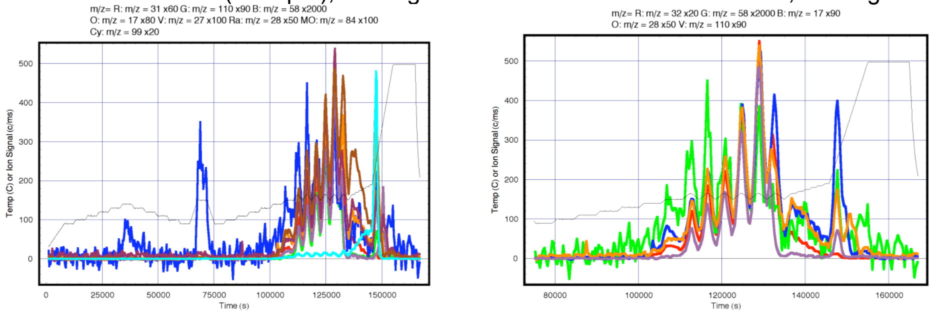


Figure 3. Comparison of ion signals representing different products formed during the thermal decomposition of TAGzT under three different confinement conditions. The temperature profile for each experiment is the same as shown in Fig. 2. The graphs in the left column compare the decomposition of TAGzT under low, high and medium confinement. The graph in the upper right shows that evolution of TAG (green) in the initial decomposition step. The second graph in the right column shows the delay between the evolution of TAG (grn) and the evolution of its four main decomposition products: NH_3, HCN, N_2, and N_2H_4. The graph in the lower right shows that evolution of the various products under medium confinement. The increase in reaction rate in each subsequent thermal cycle illustrates the complex reaction network of the TAGzT decomposition.

on the surface of the TAGzT particles) that catalyzes the decomposition of TAG to the lower molecular weight gaseous species.

The protocol illustrated here for TAGzT is applied to evaluate other TAG-based compounds to assess reactions in the network that are relevant to performance, safety, manufacture, and long-term stability change as a function of molecular and physical properties of the various TAG compounds. The compounds examined in to date are TAGCl, TAGN and TAG-TATTz (supplied by Bill Koppes -- Navy/IH). The entire evaluation performed here was done with small quantities of material, less than 20 mg total for all experiments with each compound.

RESULTS AND DISCUSSION

In our evaluation of TAGzT, TAGN, TAG-TATTz and TAGCl, we assessed relative amounts of hydrazine formed from the decomposition of each compound, the extent of reaction of each compound with RDX, and the onset of decomposition to assess relative stability. A summary of these results is presented in Table I.

Table I. Hydrazine formation rates & Interaction with RDX

#	**Experiment**	**Compound**	**NH3 m/z =17**	**N2H4 m/z= 32**	**N2H4/ (NH3+N2H4)**	**H2O m/z=18**	**N2O.. m/z=44**	**burning rate (% increase)**
1	TAGzT009	TAGzT	15	46.4	75.57%	1.14	0.00	
2	TAGTATT004	TAG-TATTz	20.36	21.7	51.59%	10.30	1.47	
3	TAGN002	TAG nitrate	34.6	10.4	23.11%	19.40	2.20	
4	TAGzT013	TAG Chloride	27.18	3.31	10.86%	1.89	0.12	
5	TAGzT024	TAGzT/RDX	11.62	0.24	2.02%	12.62	16.1	226
6	TAGTATTz003	TAG-TATTz/RDX	14.67	0.23	1.54%	9.95	14.73	165
7	TAGN003	TAG nitrate/RDX	9.44	0.11	1.15%	16.7	14.55	
8	TAGzT051	TAG Chloride/RDX	6.25	0.042	0.67%	16.59	19.62	

* Units for ion signal value columns are percent of total ion signal in the time region associated with decomposition of the TAG salt.

The numbers are the ratio of N_2H_4 signal to the sum of N_2H_4 and NH_3.

The fraction of the total ion signal representing NH_3, N_2H_4, H_2O and N_2O are shown for each experiment. To assess the production rate of hydrazine from each compound, the ratio of N_2H_4 to the total nitrogen containing compounds released from TAG (NH_3 and N_2H_4) is shown in column 6. The results from experiments with the four TAG salts by themselves are shown in lines 1 through 4 and the results from experiments in which each TAG salt is mixed with RDX is shown in lines 5 through 8.

DECOMPOSITON OF TAG SALTS

The experiments with the TAG salts by themselves show that TAGzT yields the largest fraction of hydrazine (~76%) and TAG chloride yields the least (~11%). The yield of hydrazine from TAG-TATTz is ~52% and the yield from TAGN is ~ 23%. Thus, the two TAG salts with simple anions yield a significantly lower fraction of hydrazine than the salts with more complex organic anions. Reaction of hydrogen from the TAG with the chloride anion to form HCl from TAGCl and with the nitrate anion to form H_2O from TAGN is observed in these experiments. This suggests that either (1) a significant portion of the hydrazine formed from the decomposition of TAG may react with the chloride or nitrate anions to reduce the amount of measured hydrazine, or (2) the anions react directly with the TAG, reducing the amount of N_2H_4 formed from the decomposition of TAG.

The results on the amount of hydrazine observed in the decomposition of the four TAG salts indicate that the Cl^- and NO_3^- anions may either react more readily with TAG than the ABT or TATTZ anions to reduce the amount of N_2H_4 formed, or they may react more rapidly with hydrazine via secondary reactions to reduce the net amount of measured hydrazine. In the first case, more hydrazine should be available from TAGzT and TAG-TATTz to react with RDX than from TAGCl and TAGN. In the second case, if hydrazine is formed in significant quantities from all four salts, and the lower amounts of measured hydrazine from the TAGN and TAGCl salts are due to secondary reactions, then it is possible that the reaction of hydrazine with RDX will be more rapid than its reaction with the anions. In this case, all of the salts may undergo significant interactions with RDX. This is examined in the next section.

REACTION OF TAG SALTS WITH RDX

Data illustrating the reactions of mixtures of RDX with TAGzT, TAG-TATTz, and TAGN are shown in Figures 4 and 5. Ion signals formed in the mass spectrometer and representing various species formed in the reaction of each TAG salt with RDX are shown in two graphs for each mixture (TAGzT/RDX in Fig. 4A and 4B, TAG-TATTz/RDX in Fig. 4C and 4D, and TAGN/RDX in Fig. 5A and 5B). The first graph in each set shows four signals that illustrate the decomposition of the TAG salt and its interaction with RDX. The signals represent N_2H_4 (m/z=32), NH_3 (17), H_2O (18), N_2O (44) and CH_2NO (44). The N_2O and CH_2NO species, formed in the reaction of TAGzT with RDX, have the same nominal m/z value. They were identified from isotopic crossover experiments using mixtures of TAGzT with the deuterium and ^{15}N isotopomers of RDX. The second graph in each set shows N_2H_4 and four of the main species observed in the thermal decomposition of RDX: oxy-s-triazine (OST), CH_2O, hexahydro-1-nitroso-3,5-dinitro-s-triazine (ONDNTA) and RDX, which have been described in previous publications.[9, 10, 14]

The ion signals representing the species can be divided into two groups of temporally related signals. One group occurs after RDX melts at ~202°C, which is indicated by the onset of evolution of OST from the sample (orange curve in Fig. 4B, 4D, and 5B). The other group occurs prior to the melting of RDX and is associated with the onset of the decomposition of the TAG salt to form N_2H_4, NH_3, HCN and N_2 (not shown). The onset of decomposition of the TAG salt is best illustrated by the signal representing N_2H_4, since its scaling factor is higher than the other

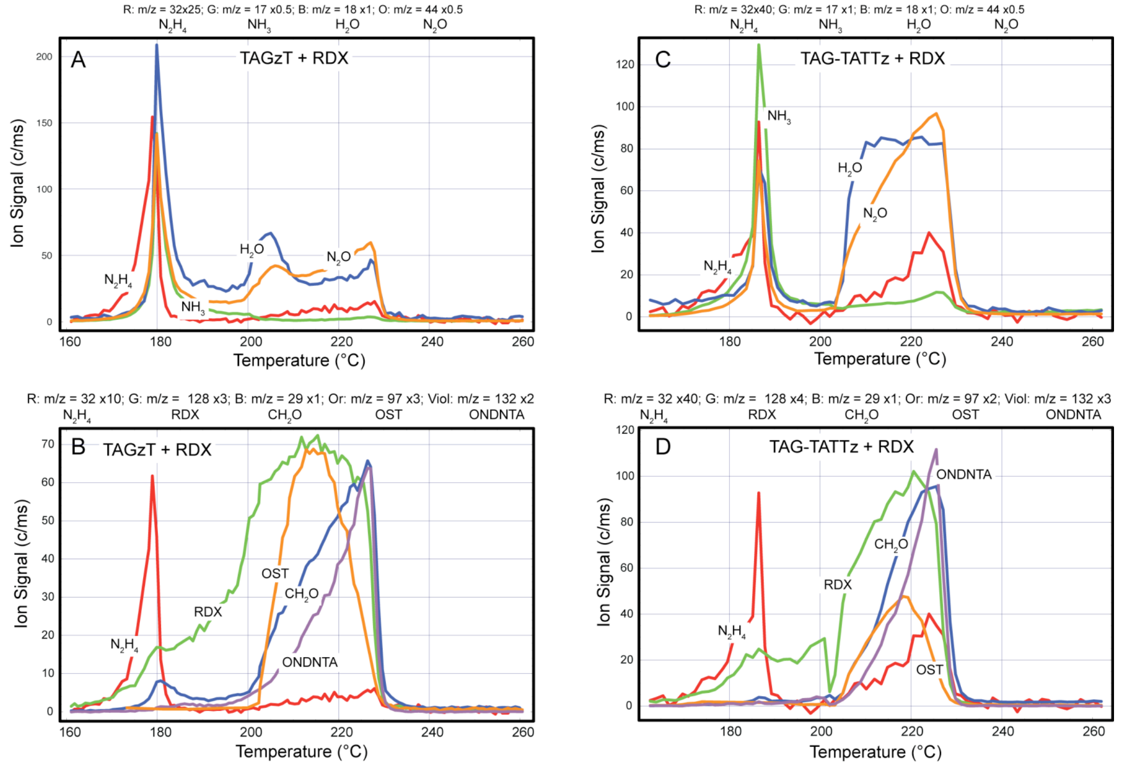


Figure 4. Ion signals representing various species formed in the decomposition of mixtures of TAGzT with RDX (A & B) and TAG-TATTz with RDX (C & D). The scaling factors and m/z values associated with each species are shown at the top of each graph. Heating rate: 2.5°C/min

species. For example, the onset of hydrazine evolution from TAGzT/RDX starts slightly above 160°C (Fig. 4B). The scaling factor for N_2H_4 is high due to its low concentration in the reaction cell caused by its interaction with RDX.[7] When RDX is not present, the signals from N_2H_4 and NH_3 are comparable.

The reaction of hydrazine with RDX is observed for the three TAG salts. In each case, signals representing H_2O (18), N_2O (44), CH_2NO (44) and NO (30, not shown) increase rapidly at the same time that the N_2H_4 signal is decreasing. These signals illustrate the reaction of hydrazine with RDX for each TAG salt. In each case, the signals representing H_2O, NH_3, N_2O/CH_2NO are large and comparable in intensity. Correspondingly, the signals representing N_2H_4 are small and comparable in each case. These results suggest that hydrazine is formed in comparable quantities from all three TAG salts and its interaction with RDX is similar in each case. This indicates that reaction of hydrazine with RDX is more rapid than its reaction with any of the three different anions. Thus, even though the amount of hydrazine observed from the thermal decomposition of TAGN is less than the other two TAG salts, its rate of reaction with any of the anion is slow compared to its reaction with RDX and its performance should not be affected by the anion in these three cases.

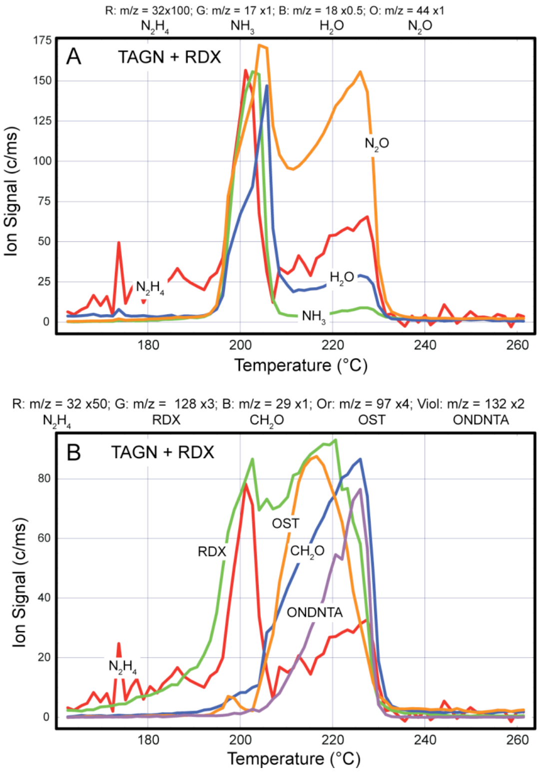


Figure 5. Ion signals representing various species formed in the decomposition of a mixture of TAGN with RDX. The scaling factors and m/z values associated with each product are shown at the top of each graph. Heating rate: 2.5°C/min.

Although the interactions of each TAG salt with RDX have many similarities, there are significant differences. The reaction with TAGzT starts at the lowest temperature (~175°C), the reaction with TAG-TATTz starts at a slightly higher temperature (~182°C), and reaction with TAGN starts at the highest temperature (~193°C). The duration of the interaction of hydrazine with RDX is the shortest for TAG-TATTz (ΔT~4°C) and greatest for TAGN (ΔT~10°C). While the reaction of hydrazine with RDX starts and finishes prior to melting of RDX for TAGzT and TAG-TATTz, it starts just prior to melting of RDX and continues past the melting point of RDX for TAGN. This behavior coupled with the similar intensities of the N_2H_4, NH_3, H_2O and N_2O/CH_2O signals for all three salts suggests that the interaction between hydrazine and RDX occurs in the gas phase.

Reaction of hydrazine with RDX in the gas phase is consistent with models of RDX decomposition in the condensed phase that show that the rate of sublimation of RDX from either the solid or liquid is four to five orders of magnitude greater than its decomposition rate in either the gas or liquid phase (see Fig. 12 in reference[9]). When RDX is present by itself, its slow reaction in the gas phase compared to its rate of sublimation and recondensation on the surface of RDX allows a quasi two-phase equilibrium to be established between the gas and condensed phases. This effectively eliminates the sublimation process as a rate limiting step in the reaction process. However, in the presence of hydrazine from the thermal decomposition of the TAG salts, reaction of RDX in the gas phase is more rapid. Thus, quasi two-phase equilibrium between RDX in the gas and condensed phases is significantly altered and the rapid rate of sublimation of RDX supplies ample amounts of RDX to react with the hydrazine.

The reaction of hydrazine with gaseous RDX does not appear to alter the subsequent decomposition of the remaining RDX from that observed when RDX is decomposed by itself.[9] In one reaction channel, RDX decomposes in the liquid phase to OST, H_2O, NO and NO_2, which start to evolve when RDX melts. In the other main reaction channel, RDX reacts with NO to form ONDNTA, which then decomposes to form CH_2O, N_2O and several other products. Both of these main reaction channels are illustrated with the data shown in Figures 4 and 5. This normal decomposition behavior is observed in the experiments with all three TAG salts.

One slight difference between the decomposition of RDX by itself and its decomposition after having been exposed to the reaction of hydrazine with the RDX is the evolution of H_2O from the RDX. In the experiments with all three TAG salts that rate of evolution of water from the sample as the RDX melts is higher than is observed in the decomposition of RDX by itself. The origin of this behavior is currently unknown. It is possible that some of the water formed in the reaction of hydrazine with RDX is absorbed by the remaining RDX and is later released upon melting.

STABILITY OF TAG SALTS

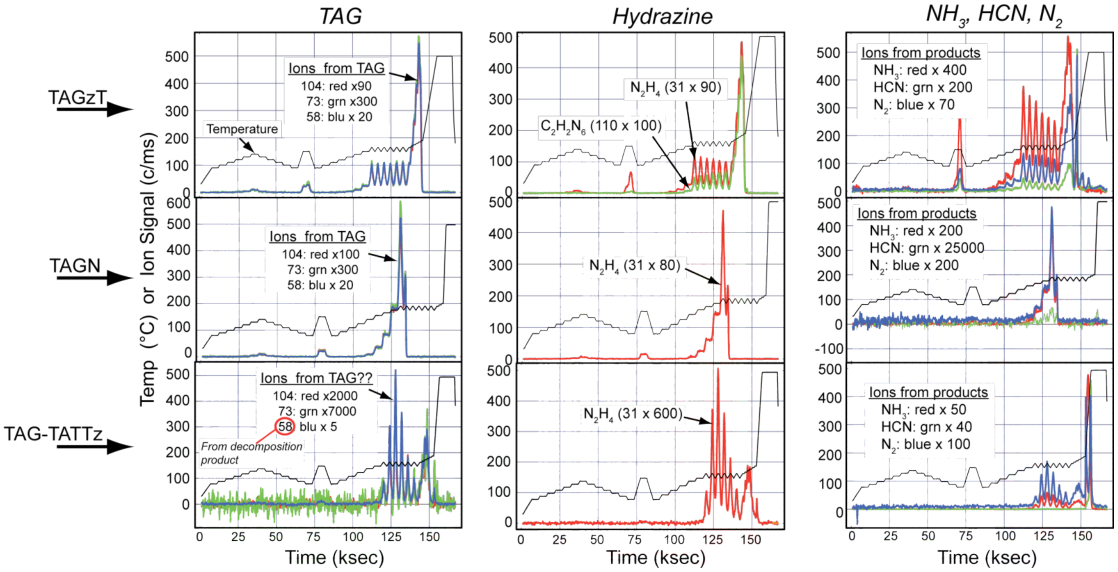


Figure 6. Comparison of TAG, hydrazine and TAG decomposition products NH_3, HCN and N_2 from three TAG salts: TAGzT, TAGN, and TAG-TATTz. The samples are analyzed using the protocol described in the methods section. Note that the lower and upper temperature limits for the thermal cycles in the TAGN experiment is higher than for the other two compounds.

Understanding the thermal stability of TAG salts and their possible interaction with other ingredients is important for assessing possible production issues and long-term aging properties of formulations. We have screened TAGzT, TAG-TATTz and TAGN. The results are shown in Figure 6. Three aspects of the thermal decomposition are examined and compared for each compound: (1) The initial decomposition step, R1 in the TAGzT mechanism (Fig. 1); (2) The decomposition of TAG to N_2H_4, NH_3, HCN and N_2, reactions R2 and R3; and (3) Whether feedback loops are established in the reaction mechanism to create an “autocatalytic-like” effect. These are examined using the thermal profiles outlined in the methods section. Comparison of ion signals representing the rates of evolution of TAG, N_2H_4 and NH_3/HCN/N_2 are shown in Fig. 6.

The results for TAGzT show the following:

1. TAG evolves from the sample (represented by ion signals at m/z values of 58, 73 and 104). 104 is the molecular ion of TAG. 73 and 58 are daughter ions in its mass spectrum. The first significant TAG signal is observed at the step to 110°C in lower confinement conditions and at the step to 120°C in the higher confinement conditions.

2. Under both high and low confinement conditions, hydrazine and the other TAG decomposition products, NH_3, HCN and N_2, first evolve at the 150°C step.
3. The rate of evolution of TAG does not accelerate dramatically under lower confinement, as indicated by the signals in the thermal cycling region shown in Fig 6. However, increasing the confinement of gaseous products causes the reaction to accelerate in the thermal cycling region (data not shown). This indicates that feedback loops, as indicated by reactions R13 and R14, are established in the decomposition process.

This data suggests that any processes associated with the manufacturing of propellant near the temperature range of 120 to 140ºC should be carefully evaluated for compatibility and safety issues, as this is the temperature region at which TAG decomposes. Furthermore, the reaction of TAG with other compounds will affect the equilibrium condition established in R1 and lead to a more rapid decomposition of TAGzT. Possible compounds may include either other ingredients used in a formulation or the emergence of new species in the reaction of TAGzT itself.

The results for TAG-TATTz show the following:

1. There is no significant mass loss or evolution of TAG from the sample as it is heated in isothermal steps to 140ºC, back down to 80ºC and then up to 150ºC.
2. TAG evolves from the sample as seen with the TAGzT. TAG is represented by ion signals at m/z values of 104, 73 and 58. The first significant TAG signal is observed at 165ºC.
3. Subsequent decomposition of the TAG to form the major lower molecular weight products, N_2H_4, NH_3, N_2 and HCN occur approximately 1000 seconds after the appearance of TAG.
4. The temporal behavior of the rate of evolution of the products in the thermal cycling region indicate the establishment of a feedback loop in the reaction mechanism that leads to an increasing rate of reaction.

The onset of the initial decomposition step in TAG-TATTz occurs at a temperature 45ºC higher than TAGzT. Thus, TAG-TATTz is more thermally stable than TAGzT.

The results for TAGN show the following:

1. The thermal decomposition of TAGN is different from the thermal decomposition of the other compounds in that the TAG and the major lower molecular weight product, N_2H_4 evolve simultaneously. In experiments with TAGzT and TAG-TATTz, the evolution of TAG and its decomposition products were separated by 1000 to 2000 seconds. This is not the case with TAGN. The products appear to be evolving at the same time.
2. The first significant TAG and hydrazine signal is observed at the step to 120ºC. Thus, the onset of decomposition of TAGN is comparable to TAGzT.
3. The rate of decomposition of TAGN in the thermal cycling region of 150 to 165°C used for TAGzT and TAG-TATTz was slower. To obtain data in the thermal cycling region of the experiment, the TAGN sample was cycled between 175 and 190°C.

The onset of decomposition of TAGN occurs at approximately the same temperature as TAGzT, 120°C.

Use of TAGzT or TAGN in a propellant that requires processing near 100°C during its production may present compatibility and possibly safety issues. In contrast, TAG-TATTz is more stable than the other two compounds and its compatibility with other ingredients may be less of a concern.

SUMMARY AND CONCLUSIONS

Reactions of compounds used as ingredients in propellant formulations play a central role in determining their performance, manufacturability, safety, IM properties and long-term aging behavior. The decomposition of individual compounds and the interaction of various ingredients in a propellant formulation form a reaction network that will determine the behavior of a propellant over the range of conditions it encounters during its life cycle. Methods to identify the elements and linkages in the reaction network and quantitatively characterize its behavior have not been available to the energetic materials community.

We are developing a new paradigm, known as "Concept, Methods and Protocols for Reaction Hierarchy and Network Development" (CoMPReHND) to address a range of reactivity issues that underlie propellant performance, safety, IM behavior and long-term aging. The CoMPReHND paradigm has been used to evaluate the thermal decomposition of four TAG-based salts and their reaction with RDX.

Previous results from experiments examining the thermal decomposition of TAGzT and its interaction with RDX showed that hydrazine is formed in abundance in the thermal decomposition of TAGzT and it reacts more rapidly with RDX than RDX can decompose by itself. In addition, it was found that onset of decomposition occurs at ~110°C and involves the dissociative sublimations of TAGzT to TAG and ABT. This presents concerns if production of the propellant requires the use of elevated temperatures.

To develop new ingredients that meet performance requirements while satisfying compatibility, safety and long-term aging issues, we are in the process of investigating a range of different compounds, which are likely to form hydrazine, to determine essential features of their reaction networks. The data presented in this paper focuses four TAG-based salts and the role that the anion plays in the net production of hydrazine from TAG, its interaction with RDX, and the onset of decomposition reactions. Four TAG-based salts were investigated: TAGzT, TAG-TATTz, TAGN, and TAGCl.

In experiments with each TAG-based salt by itself, it was found that the relative fraction of N2H4 observed from the four compounds ranged from 11% for TAGCl, 23% for TAGN, 52% for TAG-TATTZ, up to 76% for TAGzT. The results show that the smaller inorganic anions react more readily with the hydrazine and/or TAG than the organic anions, as may be expected.

In experiments with mixtures of each TAG-based salt and RDX, it was found that the extent of interaction of TAGzT, TAG-TATTz, and TAGN were similar (TAGCl was not included in the experiments with RDX). Thus, it is likely that each compound forms comparable amounts of hydrazine that is able to react with RDX faster than it reacts with any of the three anions. In addition, the reaction of hydrazine from TAGzT and TAG-TATTz occurs below the melting point of RDX, whereas the reaction of hydrazine from TAGN occurs near and above the melting point of RDX. The similarity in the observed rates of reaction in all three cases indicates that the hydrazine reacts with RDX in the gas phase. It is interesting to note that consumption of RDX in the gas phase by reaction with hydrazine will reduce the rate of condensation of RDX from the gas to solid or liquid, which has the effect of increasing the net rate of transport of RDX from the condensed phase to the gas phase.

The onset of decomposition of TAGzT, TAG-TATTZ, and TAGN was examined. TAGzT and TAGN both decompose to form TAG with an observed onset temperature for each between 110 and 120°C. The onset temperature for onset of reaction of TAG-TATTz occurs at about 165°C, which is approximately 45°C above the other two compounds.

The results illustrate the utility of using the CoMPReHND paradigm to examine the reaction networks that control the decomposition and interactions of energetic compounds used in propellant formulations. In this paper CoMPReHND has been used to identify and probe the initial reactions that control the behavior of a group of related compounds. It is effectively used as a screening tool. Once more promising compounds are identified, CoMPReHND can be used to more fully understand the reaction network and quantitatively characterize its behavior over a range of environmental conditions encountered during its life cycle.

FUTURE WORK

A series of new compounds targeted at forming hydrazine, synthesized by Phil Pagoria (LLNL) and David Chavez (LANL), will be examined in future work.

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