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13. ABSTRACT (Maximum 200 words) A summary of the most important findings on the thermal decomposition of five cyclic nitramines is presented. The compounds studied include: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-s-triazine (RDX), hexahydro-1-nitroso-3,5-dinitro-s-triazine (ONDNTA), 1,3,5-trinitro-1,3,5-triazacycloheptane (TNCHP), and 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K6). The thermal decomposition processes were studied using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) to identify the decomposition products and to determine their gas formation rates and using mixtures of isotopically labeled analogues of the compounds to track the decomposition mechanisms by analyzing the extent of isotopic scrambling and the deuterium kinetic isotope effect (DKIE). Extensive results on the thermal decomposition of RDX and HMX in the solid and liquid phases show that their decomposition is controlled by several parallel decomposition pathways. One pathway involves the loss of HONO and the formation of oxy-s-triazine (OST) from the RDX ring. The other pathway occurs via the mononitroso intermediate of the parent compound. The decomposition of the mononitroso-RDX intermediate, ONDNTA, has been extensively studied and a summary of the highlights of its decomposition is presented. The results on TNCHP show that it is the only one of the cyclic nitramines studied that is stable in the liquid phase. It does not appear to decompose via loss of HONO from its ring as is seen in the decomposition of RDX and HMX in the liquid phase. Preliminary impact studies on TNCHP indicate that it is slightly less sensitive than TNT. The decomposition of K6 shows that replacing a methylene group in the RDX ring with a keto group destabilizes the compound.

14. SUBJECT TERMS Thermal decomposition, thermal stability, mass spectrometry, isotopic labels, deuterium kinetic isotope effect, DKIE, nitramines, nitroso compounds, cyclic nitramines, HMX, RDX, K6, TNCHP, ONDNTA, kinetics, reaction mechanisms, reaction rates, sensitivity, explosives, propellants, energetic materials. 15. NUMBER OF PAGES 10 16. PRICE CODE

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INSENSITIVE ENERGETIC MATERIALS: THE  
IMPORTANCE OF PHYSICAL PROPERTIES AND  
MOLECULAR STRUCTURE

FINAL REPORT

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DECEMBER 22, 1993

U. S. ARMY RESEARCH OFFICE

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## FOREWORD

This project was undertaken to further our understanding of the reaction mechanisms that control the thermal decomposition of energetic materials, specifically cyclic nitramines, and from this understanding provide insight into how these reaction mechanisms may lead to differences in the sensitivity of these materials to heat, impact and shock. Throughout the course of this work we have had extensive collaborations with Dr. Suryanarayana Bulusu (ARDEC) which have been a major factor in contributing to the success of this project. His synthesis of the isotopically labeled compounds used in our experiments and our discussions on the thermal decomposition results has led to significant advances in the understanding of how these materials behave.

This report summarizes the most important results obtained on the thermal decomposition of five different cyclic nitramines. The reader is referred to the publications associated with the work conducted on this project that are listed in Section III of this report.

## I. Statement of the Problem

The purpose of this project has been to further our understanding of the chemical reaction mechanisms that control the thermal decomposition of cyclic nitramines, with the future goal of applying this knowledge to predict the behavior of these materials when subjected to heat, impact or shock. Since HMX and RDX are widely used in explosives and propellants, the first part of this project concentrated on understanding the decomposition of these two materials in the solid and liquid phases. In the second part of the project, the decomposition of reaction intermediates identified in the decomposition of RDX and HMX along with other cyclic nitramines with physical properties and molecular structures different from RDX and HMX have been studied to determine how these changes affect the reaction mechanisms that control their decomposition. The objective is to determine which properties and structures are important in controlling the decomposition of these materials so that better materials can be synthesized and used in new energetic material formulations.

To obtain this information we have used the simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS) system<sup>1</sup> to obtain the identities and gas formation rates of the thermal decomposition products formed as the nitramines are heated. To determine the details of the bond-breaking and bond forming steps in the decomposition process, we have utilized mixtures of isotopically labeled analogues of the cyclic nitramines to determine the deuterium kinetic isotope effect (DKIE) and extent of isotopic scrambling in the reaction products.

## II. Summary of Most Important Results

The structures of the compounds that have been studied in this project are shown in Figure 1. These compounds include: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); hexahydro-1,3,5-trinitro-s-triazine (RDX); the mononitroso analogue of RDX, hexahydro-1-nitroso-3,5-dinitro-s-triazine (ONDNTA); a compound similar to RDX except with one additional CH<sub>2</sub> group in the ring, 1,3,5-trinitro-1,3,5-triazacycloheptane (TNCHP); and a compound with a C=O group in place of a CH<sub>2</sub> group, 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K6). The compounds studied most extensively in this project are RDX and HMX in which detailed quantitative information on their decomposition behavior has been obtained.<sup>2-4</sup> ONDNTA, TNCHP and K6 have also been studied extensively<sup>5,7</sup> but at the time of the conclusion of this project only qualitative descriptions of their decomposition behavior have been obtained. Several other cyclic dinitramines were examined briefly in the beginning of the project and it was deemed that further studies of these materials had a lower priority and thus, no further work was performed on these materials.

The following sections summarize the main results that were obtained on each of these compounds.

### II.1 RDX RESULTS.

Through the use of STMBMS measurements, time-of-flight

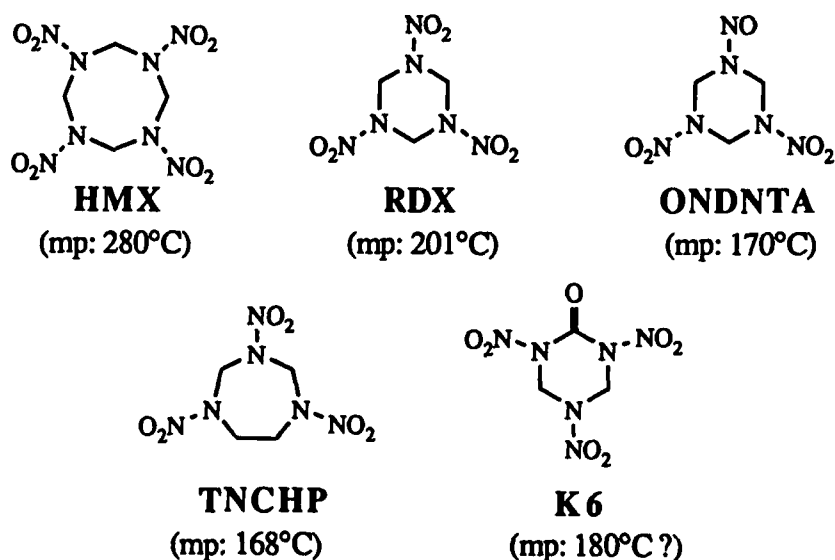
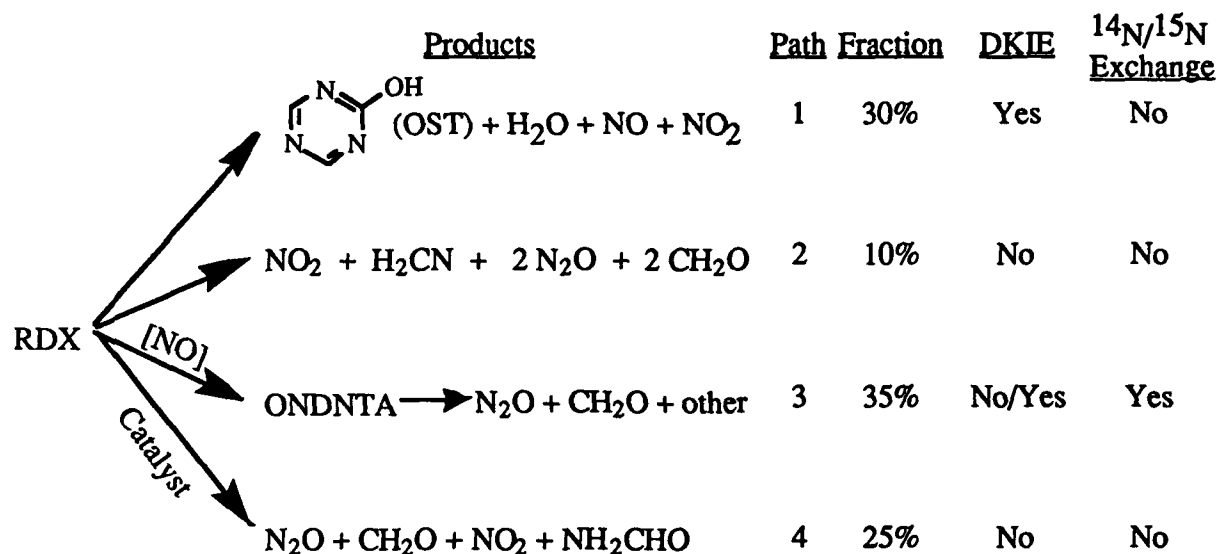


Figure 1. Cyclic nitramines that were studied in this project.

(TOF) velocity spectra analysis, and  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{18}\text{O}$  labeled analogues of RDX, the thermal decomposition products of RDX have been identified as  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{CO}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_2\text{CHO}$ ,  $\text{NO}_2$ ,  $\text{HONO}$ ,  $(\text{CH}_3)\text{NHCHO}$ , oxy-s-triazine (OST), and ONDNTA.<sup>2,3</sup> By measuring the temporal behaviors of the gas formation rates of each of these products during the course of a decomposition experiment, the existence of four primary reaction pathways that control the decomposition of RDX in the condensed phase have been discovered.

In the liquid phase, the four primary reaction pathways that control the decomposition of RDX are:



These reaction pathways consist of two pathways that are first order reactions solely in RDX, suggesting that these are unimolecular decomposition routes. Of these two pathways, one produces predominantly OST,  $\text{NO}$ , and  $\text{H}_2\text{O}$  and accounts for approximately 30% of the decomposed RDX, and the other produces predominantly  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  with smaller amounts of  $\text{NO}_2$ ,  $\text{CO}$ , and  $\text{NH}_2\text{CHO}$  and accounts for 10% of the decomposed RDX. The third pathway consists of formation of ONDNTA by reaction between  $\text{NO}$ , produced in the first decomposition pathway, with the amino radical, produced after scission of the  $\text{N}-\text{NO}_2$  bond in RDX, and the subsequent decomposition of ONDNTA to predominantly  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$ . The fourth reaction pathway consists of decomposition of RDX through reaction with a catalyst that is formed from the decomposition products of previously decomposed RDX. The third and fourth reaction channels each account for approximately 30% of the decomposed RDX.

The formation of  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  via the other unimolecular decomposition channel (2) is consistent with both  $\text{N}-\text{NO}_2$  bond breaking followed by the subsequent decomposition of the remaining fragment to  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$ , possibly via the  $\text{CH}_2=\text{N}-\text{NO}_2$  intermediate, and also via the concerted symmetric triple fission of RDX to three  $\text{CH}_2=\text{N}-\text{NO}_2$  fragments and their subsequent decomposition to  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$ . However, the formation of  $\text{CH}_3\text{NHCHO}$  may possibly originate by reaction of  $\text{CH}_2\text{O}$  with the  $\text{H}_2\text{CN}$  radical left from the unraveling of the RDX ring after the breaking of the  $\text{N}-\text{NO}_2$  bond. Thus indicating that the  $\text{N}-\text{NO}_2$  bond breaking channel may be the more likely explanation for this reaction channel.

Our experiments with solid-phase RDX have shown that its decomposition rate is much slower than that of liquid-phase RDX. ONDNTA is the only product that appears to be formed during the early stages of its decomposition. As the decomposition of solid RDX continues,  $\text{N}_2\text{O}$  and smaller amounts of  $\text{CH}_2\text{O}$  start to evolve from the sample. After the evolution rate of these two products

increases, the products associated with the liquid-phase RDX decomposition appear and their rate of gas formation rapidly increases. This strongly suggests that the decomposition of solid RDX occurs through formation of ONDNTA within the lattice, the subsequent decomposition of ONDNTA within the lattice to  $N_2O$  and  $CH_2O$ , followed by the dispersion of  $CH_2O$  in the RDX leading to its eventual liquefaction and the onset of the liquid-phase decomposition reactions.

The results from isotope crossover experiments with RDX and the observed deuterium kinetic isotope effects (DKIE) lend further support for the four primary decomposition pathways described above.

The lack of isotopic scrambling and the presence of a primary DKIE in OST support a unimolecular mechanism in Pathway 1. The primary DKIE in the formation of OST shows the importance of intramolecular hydrogen transfer in the rate limiting step that controls Pathway 1.

Reaction Pathway 3 is supported by the scrambling of the  $^{14}N/^{15}N$  in the nitroso group of the ONDNTA formed during the decomposition of RDX. In addition, the lack of a DKIE in the formation of ONDNTA also supports this pathway. Furthermore, the presence of H/D scrambling is consistent with the presence of more labile hydrogen on the neighboring carbon atom of the N-NO group in ONDNTA.

The lack of nitrogen scrambling in  $N_2O$  is consistent with the conclusion that methylene nitramine collapses to  $N_2O$  and formaldehyde without cleavage of the N-N bond. However, the lack of direct evidence of methylenenitramine makes its formation through this intermediate uncertain.

The lack of a DKIE in the formation of  $CH_2O$  supports the conclusion that hydrogen is not involved in the rate limiting steps of Pathways 2, 3 and 4 that lead to its formation. However, since NO is produced via Pathway 1, the rate of formation of ONDNTA from RDX in Pathway 3 does exhibit an indirect DKIE.

Unlike the case of HMX decomposition which is catalyzed by  $H_2O$ , there seems to be no evidence of autocatalysis by  $H_2O$  in the RDX case.  $H_2O$  formation is not the sole contributor to the observed DKIE as in the case of HMX. It is, therefore, apparent that the decomposition details of RDX and HMX in our experiments are significantly different due to the fact that the former occurs in the liquid phase and the latter in the solid phase. Furthermore, RDX undergoes isotopic scrambling of nitrogen in the formation of ONDNTA, whereas for the analogous compound in HMX, ONTNTA, only 25% of the molecules are formed by mixing of the nitrogen isotopes. This implies that the formation of ONTNTA in HMX is influenced by the "cage effect" in its solid state decomposition, whereas the formation of ONDNTA in RDX occurs in the liquid phase and the "cage effect" does not play a role. This also predicts that if HMX is decomposed above its melting point, it also would exhibit more scrambling of the nitrogen isotopes.

## II.2 HMX RESULTS

The temporal behaviors of the rates of gas formation and gas release of the pyrolysis products from HMX show that the mechanisms controlling the identity and release of gas products from the particles is due to complex physicochemical mechanisms.<sup>4,5</sup> The formation of bubbles within the solid HMX particles is apparent from both the temporal behaviors of the rate of gas release of the different pyrolysis products and the macroscopic and microscopic morphology of the polymeric nonvolatile residue formed during the decomposition. The transmission electron micrographs (TEM) of the nonvolatile residue (NVR) show that the NVR consists of broken ellipsoidal shells that are probably the remnants of bubbles that had formed within the HMX particles. Simple arguments indicate that the pressure of the gases within the bubbles ranges up to 9 MPa and may

range up to 240 MPa depending on the strength of the solid HMX at the decomposition temperature.

The identity of the pyrolysis products and their temporal behaviors indicates that at least two different general reaction schemes are producing products. The first one, which is operational by itself during the induction stage of the decomposition and concurrently during the other stages, produces  $N_2O$  and  $CH_2O$  at approximately equal rates and appears to depend on the surface area of the HMX. The second scheme, whose products first appear at the start of the acceleratory stage, produces a wider range of products with varying ratios of gas release rates during the decomposition. The second reaction scheme is associated with the formation of the bubbles and produces  $N_2O$ ,  $H_2O$ ,  $CH_2O$ ,  $NO$ , and  $CO$  in larger quantities and  $HCN$ ,  $(CH_3)NHCHO$ ,  $(CH_3)_2NNO$ ,  $ONTNTA$ , and the  $NVR$  in lesser quantities. Thermal decomposition of the  $NVR$  indicates that it is a form of a polyamide. The formation of the relatively high concentration of water and the polyamide film early in the acceleratory stage of the decomposition is consistent with the reactions of the second scheme occurring in the high pressure bubbles.

The second reaction scheme emphasizes the complex nature of the physical processes occurring during the decomposition. Most of the products observed during the decomposition are formed in

## Decomposition of an HMX Particle

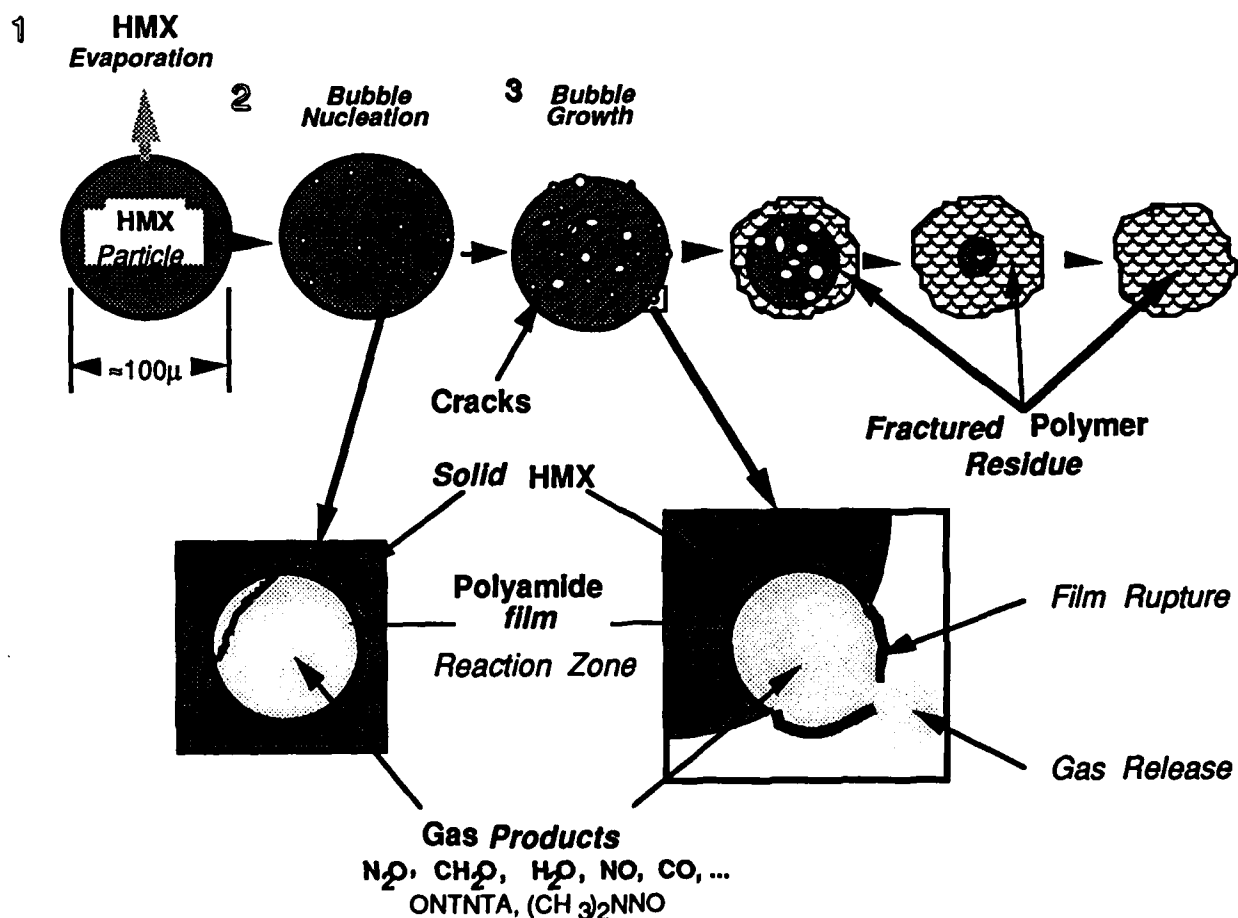


Figure 2. Physical processes involved in the thermal decomposition of HMX in the solid phase.

this reaction scheme. Under the high pressure conditions in which the products are formed, a reaction environment is created that can affect, and perhaps control, the HMX decomposition. This environment consists of a polyamide film at the interface of HMX and high pressure gaseous products. The relatively large concentration of water indicates that the reactions occur in a high temperature aqueous environment. A schematic diagram of the decomposition sequence of an HMX particle is shown in Figure 2. The sequence involves the nucleation and growth of bubbles within the HMX particle, leading to the fracture and subsequent release of gaseous products.

Thermal decomposition experiments with deuterium,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{18}\text{O}$  isotopic analogues of HMX have been used to investigate the decomposition mechanism of HMX. By determining the extent of isotopic scrambling in each decomposition product and examining the DKIE on the rates of formation of the various products, several conclusions have been drawn about the HMX decomposition mechanism in the solid phase. First, the reaction pathway in which the N-N bond breaks forming  $\text{NO}_2$ ,  $\text{H}_2\text{CN}$ , and three methylenenitramine intermediates that subsequently decompose into  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  is consistent with the lack of hydrogen isotope scrambling in  $\text{CH}_2\text{O}$ , the lack of nitrogen isotopic scrambling in  $\text{N}_2\text{O}$ , and the scrambling of only one C-N bond in the formation  $(\text{CH}_3)\text{NHCHO}$ . Second, the DKIE clearly shows that there is another decomposition channel in which the rate limiting step involves hydrogen atom transfer. Comparison of differences in the DKIE in experiments run on mixtures of HMX-ul and HMX-d8 that were mixed either mechanically or in solution, suggests that the reaction mechanism involves transfer of a hydrogen atom to the HMX rather than abstraction of hydrogen from the HMX. Third, the lack of complete isotopic scrambling of the N-NO bond in ONTNTA shows that some decomposition does occur in the HMX lattice and that a 'cage effect' may play some role in the decomposition of HMX. Finally, the results are consistent with an autocatalytic mechanism in which water trapped within the HMX particles acts as the catalyst. The results show that the decomposition of HMX in the condensed phase is a complex process that involves several different reaction branches.

### II.3 ONDNTA RESULTS

To determine further details on the reaction mechanisms that control the decomposition of the mononitroso intermediates formed in the decomposition of RDX and HMX, we have studied the decomposition of ONDNTA.<sup>6</sup> The results have shown that ONDNTA decomposes in two distinct temperature regions. One is between  $110^\circ\text{C}$  and  $145^\circ\text{C}$  and the other is between  $155^\circ\text{C}$  and  $210^\circ\text{C}$ . The extent of decomposition in the lower temperature region depends on the degree of containment of the gaseous species, with higher containment causing greater decomposition in the lower temperature channel. Under the highest degree of containment the entire sample decomposed in the lower temperature channel. The major products formed during the thermal decomposition of ONDNTA are  $\text{CO}$  or  $\text{N}_2$ ,  $\text{CH}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_2$  in both the lower and higher temperature regions. Depending on the degree of containment within the reaction cell, various amounts of other decomposition products are observed. For low degrees of containment, in which approximately 2% to 10% of the sample decomposes in the low temperature channel, small amounts of formamide ( $\text{NH}_2\text{CHO}$ ), N-methylformamide ( $\text{CH}_3\text{NHCHO}$ ) and N,N-dimethylformamide ( $(\text{CH}_3)_2\text{NCHO}$ ) are observed. For high degrees of containment, in which all of the ONDNTA decomposes in the low temperature channel, large amounts of water and dimethylnitrosamine,  $(\text{CH}_3)_2\text{NNO}$ , are also formed. In addition, the mass spectra of the products indicate that either the  $\text{CH}_2\text{NCH}_2$  radical or  $\text{CH}_3\text{NCH}_2$  is formed at amounts comparable to  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  in the higher temperature channel. Isothermal experiments in the low temperature channel show that the fraction of the sample that decomposes in this channel is fixed and the fraction depends on the degree of containment. This behavior is quite unusual and further experiments are being performed to uncover its cause. The temporal behavior of the rates of formation of the products in the higher temperature channel also show that autocatalysis plays a significant role in the reaction mechanism for this channel.



The correlation of the formation of these products from the thermal decomposition of ONDNTA with those that we have observed in our previous experiments with RDX and HMX is consistent with the mononitroso analogue being an important intermediate that controls the identity and rates of formation of the products formed in the decomposition of RDX and HMX.

#### II.4 TNCHP RESULTS

The decomposition of TNCHP<sup>7</sup> has not been investigated as thoroughly as HMX, RDX or ONDNTA. However, we have found several interesting results in our experiments on TNCHP. We have found that TNCHP is much more stable in the liquid phase than either RDX or HMX. TNCHP melts at 170°C but does not show the first evidence of decomposition until ~205°C and only starts to decompose at more rapid rates above 240°C. The major products formed in its decomposition are CH<sub>2</sub>O and N<sub>2</sub>O. Products formed to a lesser extent include: H<sub>2</sub>O, HCN, NO, and NO<sub>2</sub>. Ion signals, representing other thermal decomposition products, are also observed. These results illustrate the increased thermal stability of TNCHP in the liquid phase compared to RDX. An ion signal at  $m/z = 146$  is analogous to the ion signal at  $m/z = 132$  that arises from ONDNTA formed in the decomposition of RDX. Therefore, the ion signal at  $m/z = 146$  most likely arises from the mononitroso analogue of TNCHP and thus decomposition via the mononitroso intermediate of TNCHP is also important in the decomposition of this compound.

In isothermal experiments with TNCHP, the temporal behaviors of the ion signals associated with the decomposition products from TNCHP are indicative of several parallel reaction pathways. Ion signals associated with processes that are approximately first order in TNCHP are associated with signals from NO and NO<sub>2</sub>. Ion signals associated with intermediate products formed during the thermal decomposition are found at  $m/z$  values of 55, 84, 130, and 146. The ion signals at  $m/z$  values of 55, 84 and 130 have temporal behaviors similar to that of 146, which probably represents the mononitroso analogue of TNCHP. This suggests that the ion signals at  $m/z$  values of 55, 84 and 130 may be ion dissociation products of the TNCHP mononitroso analogue.

Finally, a stable product, similar to the formation of OST in the decomposition of RDX, is not observed in the thermal decomposition of TNCHP. This inability to form a decomposition product by stabilizing the ring of the cyclic nitramine may lead to the increased thermal stability of TNCHP.

#### II.5 K6 RESULTS

The decomposition of K6 is quite different from the other cyclic nitramines used in these studies.<sup>7</sup> In addition to its lower thermal stability, K6 also produces fewer and simpler decomposition products. The decomposition products from K6 are mainly CH<sub>2</sub>O, N<sub>2</sub>O and CO<sub>2</sub>, with minor contributions from HCN, CO, NO and NO<sub>2</sub>. Unlike the other cyclic nitramines used in this study, K6 does not form any amides, mononitroso analogue, or residue.

The decomposition of K6 may be initiated by attack of one of the NO<sub>2</sub> oxygen atoms on the keto group carbon atom leading to the initial elimination of CO<sub>2</sub> and followed by the rapid transformation of the remaining fragment into CH<sub>2</sub>O and N<sub>2</sub>O. The rate of decomposition of K6 through this initial four center C-N-N-O complex would appear to be competitive with N-NC<sub>2</sub> bond breaking in that no mononitroso analogue or amides are observed in the decomposition of K6.

### III. LIST OF PUBLICATIONS AND TECHNICAL REPORTS

- R. Behrens, "Thermal Decomposition of Energetic Materials: Temporal Behaviors of the Rates of Formation of the Gaseous Pyrolysis Products from Condensed-Phase Decomposition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)., J. Phys. Chem., **94**, 6706 - 6718, (1990).
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- R. Behrens, T. Land, S. Bulusu, "Thermal Decomposition Mechanisms of 1-Nitroso-3,5-dinitro-s-triazine (ONDNTA)", Proceedings of 30th JANNAF Combustion Meeting, Monterey, CA, November 1993.

### IV. LIST OF PARTICIPATING PERSONNEL

Richard Behrens, Jr , Sandia National Laboratories  
Suryanarayana Bulusu, ARDEC

### V. REPORT OF INVENTIONS

No inventions have been reported as a result of this work.

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- <sup>3</sup> R. Behrens, Jr. and S. Bulusu, **96**, 8891, (1992).
- <sup>4</sup> R. Behrens, Jr., **94**, 6706, (1990).
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- <sup>7</sup> a) R. Behrens, Jr. and S. Bulusu, *Mat. Res. Soc. Symp. Proc.*, Vol. 296, p. 13, 1993. b) R. Behrens, Jr. and S. Bulusu, *Proceedings of the 29th JANNAF Combustion Meeting*, Langley, Virginia, 1992.