

# THERMAL DECOMPOSITION OF HMX AND RDX: DECOMPOSITION PROCESSES AND MECHANISMS BASED ON STMBMS AND TOF VELOCITY-SPECTRA MEASUREMENTS\*

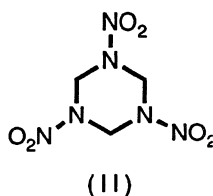
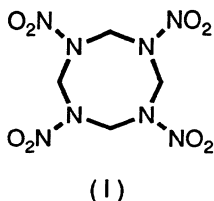
RICHARD BEHRENS  
*Sandia National Laboratories  
Combustion Research Facility  
Livermore, CA 94551-5000  
USA*

**ABSTRACT.** A brief history of the decomposition of HMX and RDX is presented to illustrate the development of the mechanisms that are used to explain the decomposition of these two nitramines. The results from simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and time-of-flight (TOF) velocity-spectra measurements on HMX and RDX are used to identify the decomposition products and to determine their gas formation rates as a function of time during the decomposition of the samples. Both nitramines form  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NO}$ , and  $(\text{CH}_3)\text{NHCHO}$  during the decomposition. RDX forms  $\text{NO}_2$  and hydroxy-s-triazine (HST), products associated with N-N bond breaking, whereas HMX forms  $\text{C}_2\text{H}_6\text{N}_2\text{O}$ ,  $\text{CO}$ , and a nonvolatile residue (NVR). A mononitroso analogue of the parent compound is formed during the decomposition of both materials. The rates of gas formation of the various pyrolysis products along with the macroscopic and microscopic features of the NVR that is generated during the decomposition of HMX suggest that a major process involved in the decomposition of HMX below its melting point is the formation of bubbles containing pyrolysis products within the HMX particles. The pressure of the gas within the bubbles may range up to 35000 psi.

Possible reaction mechanisms that include both the physical location of the reactions and the possible chemical reaction pathways are presented. The results from the STMBMS experiments are consistent with initial fragmentation of the N-N bond of the molecule to form  $\text{NO}_2$  and the subsequent unravelling of the remaining ring to form  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$ . Secondary reactions of the primary decomposition products that occur within the particles are important in determining the identity and the relative rates of gas release of the products from the solid particles. The possible bimolecular reactions between pyrolysis products and HMX are also presented.

## Introduction

The cyclic nitramines, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine HMX (I) and hexahydro-1,3,5-trinitro-s-triazine RDX (II),



are energetic ingredients that are used in various propellants and explosives. Understanding the complex physicochemical processes that underlie the combustion of these materials can lead to methods for modifying the propellant and explosive formulations in order to obtain better ignition, combustion, or sensitivity properties. A number of new experimental and diagnostic techniques, such as planar laser induced fluorescence (PLIF), coherent anti-stokes raman spectroscopy (CARS), and infrared multiphoton dissociation (IRMPD), are available to probe the gas phase processes and further the understanding of the gas phase chemistry. Similarly, the development of simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and time-of-flight (TOF) velocity-spectra techniques<sup>1,2,3</sup> have enhanced the application of mass spectrometry to probe processes in the condensed phase using evolved gas measurements.

An important goal of these new experiments is to develop a link between the physical properties and molecular structures of different nitramines and their combustive behavior. The motivation of the work on the condensed phase is to obtain a better understanding of the physical processes and reaction mechanisms that occur, so that the identity and rate of release of the pyrolysis products can be predicted, as a function of pressure and heating rate, based on the physical properties and molecular structure of the material. This information can then be used along with the gas-phase reaction models to correlate modifications of the nitramine ingredients with variations in the overall combustion.

Over the past 40 years many studies have been conducted on the decomposition of HMX and RDX under various conditions. Recent reviews of the decomposition and combustion,<sup>4,5</sup> thermal decomposition,<sup>6</sup> and summaries of possible decomposition mechanisms,<sup>6,7</sup> have been published for these materials. Based on many of these results and the structural similarities of HMX and RDX, the same decomposition mechanisms have been proposed for both materials.

Robertson's<sup>8</sup> results on the decomposition of RDX show that in solutions of dicyclohexylphthalate and trinitrotoluene (TNT) the decomposition exhibits a unimolecular behavior, whereas, neat RDX and HMX show an effect of neighboring molecules. Post analysis of the gases evolved in his experiments show the presence of: NO, N<sub>2</sub>O, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>2</sub>O, and H<sub>2</sub>O. This work provides the initial evidence that the decomposition of HMX and RDX occurs by transfer of an oxygen atom from the NO<sub>2</sub> group to the CH<sub>2</sub> group.

Subsequent mass spectral analysis of the decomposition products from HMX below its melting point, by Bulusu and Graybush,<sup>9</sup> show the same products as observed by Robertson.<sup>8</sup> In addition, they found that the rate of formation of the products varied during isothermal decomposition experiments in a way that can be explained by either the characteristic induction, acceleratory, and decay stages associated with solid-phase decompositions or by invoking autocatalytic behavior. Furthermore, <sup>15</sup>N-tracer studies<sup>10</sup> indicate that the N<sub>2</sub>O is formed without N-N bond breaking, thus, suggesting that oxygen atom transfer to the CH<sub>2</sub> group and C-N bond rupture is an important step in the decomposition. However, since the total nitrogen is not accounted for in these experiments, N-N bond breaking cannot be ruled out as the initial step in the decomposition.

A deviation from the oxygen atom transfer mechanism comes from the RDX experiments of Rauch and Fanelli<sup>11</sup> in which they observe the formation of NO<sub>2</sub> in addition to the products observed by Robertson<sup>8</sup> and Bulusu.<sup>9</sup> Their results suggest that the NO<sub>2</sub> is formed in the gas-phase decomposition of RDX.

More recent work on the decomposition of RDX<sup>12</sup> and HMX<sup>13</sup> report additional decomposition products. These products include formic acid, ammonia, and hydroxymethyl formamide from RDX<sup>12</sup> and HMX.<sup>13</sup> Observations of these products imply that the decomposition mechanism leading to the formation of the pyrolysis products is more complicated than only unimolecular