

## MASS SPECTROMETRIC INVESTIGATION OF THE THERMAL DECOMPOSITION OF RDX

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The products of thermal decomposition of 1,3,5-trinitrohexahydro 1,3,5-triazine (RDX) in vacuum have been determined mass spectrometrically below and above the melting point. Employing a cell with an elongated orifice to form a collimated beam, RDX decomposition products were identified within a few microseconds after leaving the cell. A major mode of the decomposition was the splitting of the RDX molecule into two unstable fragments at 148 and 74 amu, as determined by mass spectrometry. These fragments underwent further decomposition into numerous smaller species. A second mode of decomposition was the removal of the NO<sub>2</sub> groups from the ring, leaving dihydro-sym-triazine as a product. No evidence of the RDX molecule was found in the vapor phase.

## 1. Introduction.

The thermal decomposition of 1,3,5-trinitrohexahydro 1,3,5-triazine, RDX, has been studied extensively. Thirty years ago Robertson [1] investigated the decomposition of RDX above its melting point and determined that the products were only small molecules, NO, N<sub>2</sub>O, H<sub>2</sub>, CO, CH<sub>2</sub>O and CO<sub>2</sub>. This analysis led to the conclusion that the mechanism of decomposition was the transfer of an oxygen atom from the dinitro group to a neighboring carbon atom, eliminating N<sub>2</sub>O and CH<sub>2</sub>O. No NO<sub>2</sub> was observed. Rauch and Fanelli [2], who conducted studies between 207 and 227°C, above the melting point, reportedly observed NO<sub>2</sub> and a number of other gaseous products, including N<sub>2</sub>O, NO, CH<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub>O and HCN. Goshgarian [3] also observed NO<sub>2</sub> and these gaseous products in an investigation between 200 and 205°C, below the melting point. Cosgrove and Owen [4], from thermal decomposition at 195°C, reported NH<sub>3</sub> and CH<sub>2</sub>O<sub>2</sub> in addition to the low-molecular-weight gases observed by Rauch and Fanelli [2] and Goshgarian [3]. Other investigators reported similar products and also determined varying activation energies [5-7].

Bradley et al. [8], employing a mass spectrometer for product identification, investigated the thermal decomposition of RDX under high vacuum below the

melting point. In addition to the low-molecular-weight products they also observed larger fragments with amu values as high as 148. They employed a two-stage cell in which the first cell was kept at 175°C, while the second cell varied from 175 to 225°C with its orifice open to the mass spectrometer. They obtained solid-phase reactions with one open cell and gas-phase reactions when both cells were used. Stals [9], in a mass spectrometer study of RDX decomposition, made accurate mass measurements of 23 species in the 27 to 112 amu range.

Goshgarian [3] inserted a glass probe containing the RDX sample directly into the quadrupole mass spectrometer ion source to minimize gas-phase reactions. He reported slightly different higher molecular-weight species below and above the melting point. The heaviest species observed was at 148 amu.

The study at this laboratory was performed to determine whether the mechanistic reaction of RDX thermal decomposition involved ring fragmentation followed by fragment decomposition to smaller molecules and radicals. An effusion cell which allowed gas-sampling times on the order of microseconds by the mass spectrometer was employed for this investigation.

## 2. Experimental

The dual vacuum chamber—quadrupole mass spectrometer used in these experiments has been described previously [10]. The RDX samples were contained in an alumina effusion cell 25 mm long, with an inside diameter of 6.8 mm; an elongated orifice 0.75 mm in diameter by 5.5 mm long was employed for beam collimation. The cell was positioned within 5 cm of the ionization chamber of the mass spectrometer, allowing species leaving the solid or liquid surface to be measured within 10  $\mu$ s or less. The alumina cell was heated by a resistance furnace and temperature measurements were made by means of thermocouples imbedded in the cell body.

The ion intensities were identified by their masses, isotopic distributions, and appearance potentials. The method of determining the mass spectrometer resolution, as well as the measurement of the isotopic abundance ratios, has been presented previously [11]. All quadrupole experimental mass discrimination effects were taken into account and the necessary corrections to ion intensity pressure relationships were made. Only the chopped, or shutterable, portion of the intensities was recorded, since the mass spectrometer was equipped with a beam modulator and a phase-sensitive amplifier.

It was necessary to ascertain with a high degree of confidence that the measured ion intensities were those from the parent species and not from the fragments of the larger molecules. Therefore, the mass spectrometer was operated at an ionizing voltage of 1 to 2 eV above the appearance potential, which in nearly all cases allows only the formation of the ion from the parent species since a fragmentation process usually occurs at higher ionization voltages [12–15]. The concentration of each species can then be obtained from a knowledge of the cross sections and other parameters,

$$n_i \propto I_i T / \sigma_i (E - A_i) S,$$

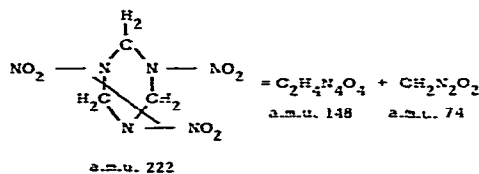
where  $n_i$  is the concentration of species  $i$ ,  $I_i$  the ion intensity for species  $i$ ,  $\sigma$  the relative cross section at the maximum of the ionization efficiency curve,  $A_i$  the appearance potential in eV,  $E$  the energy of ionizing electrons in eV,  $S$  the multiplier efficiency, corrected for molecular beam effects if necessary, and  $T$  the absolute temperature. The resolution of the

mass spectrometer is 1 in 500 and details have been given previously [11].

## 3. Discussion

Employing the techniques described in section 2, mass spectrometric studies were made below and above the melting point of 204.5°C. Fig. 1 shows the peaks observed below the melting point at amu values of 28, 30, 42, 44, 46, 56, 74 and 83. Fig. 2 depicts the peaks at 28 to 74 and fig. 3 shows peaks appearing in the range 82 to 148, all above the melting point, at 220°C. The species observed in these studies are in agreement, for the most part, with those previously reported from mass spectrometric investigations [3,8,9].

The arrival of the two large fragments of RDX at the mass spectrometer in several microseconds supports a mechanism in which the molecule undergoes fragmentation by splitting into two parts at 148 and 74 amu:



These two fragments are unstable species and thus will rapidly fragment to smaller particles. The observation of the 75 amu peak by previous investigators [3,8] would indicate the addition of an H atom by the 74 amu fragment,  $\text{CH}_2\text{N}_2\text{O}_2$ , to form the more

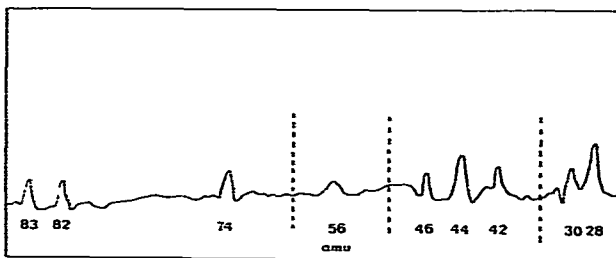


Fig. 1. Decomposition of RDX below the melting point at 200°C; amu range 28–83; mass spectrometric peaks correspond to: 28 = CO, 30 =  $\text{CH}_2\text{O}$  and NO, 42 =  $\text{C}_2\text{H}_4\text{N}$ , 44 =  $\text{N}_2\text{O}$ , 46 =  $\text{NO}_2$ , 56 =  $\text{C}_2\text{H}_4\text{N}_2$ , 74 =  $\text{CH}_2\text{N}_2\text{O}_2$ , 82 =  $\text{C}_3\text{N}_3\text{H}_4$  and 83 =  $\text{C}_3\text{N}_3\text{H}_5$ .

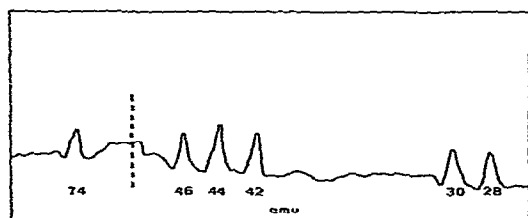
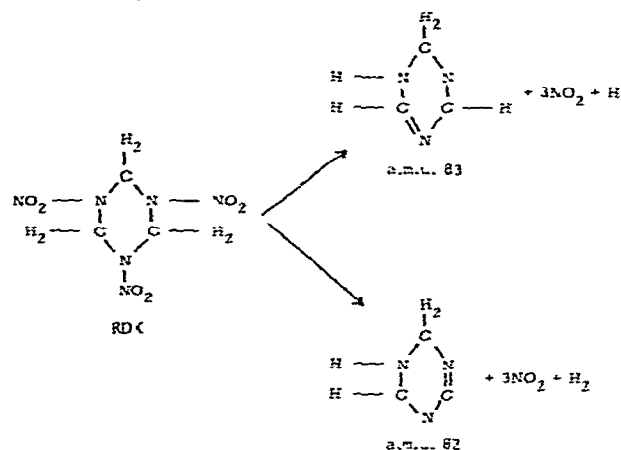


Fig. 2. Decomposition of RDX above the melting point at 220°C; amu range 28–74; mass spectrometric peaks correspond to: 28 = CO, 30 = CH<sub>2</sub>O, 42 = C<sub>2</sub>H<sub>4</sub>N, 44 = N<sub>2</sub>O, 46 = NO<sub>2</sub> and 74 = CH<sub>2</sub>N<sub>2</sub>O<sub>2</sub>.

stable molecule, CH<sub>3</sub>N<sub>2</sub>O<sub>2</sub>. The largest gaseous fragment observed in these studies, at 148 amu, confirms the results of previous experimental investigations [3,8].

The strong peaks at 82 and 83 amu found in this and previous studies indicate a second mode of decomposition in which the ring is stripped from its NO<sub>2</sub> group, forming dihydro-sym-triazine as well as a number of low molecular weight species. Two peaks at 82 and 83 are seen as a result of the RDX ring stripping of two NO<sub>2</sub> groups:



In this decomposition the NO<sub>2</sub> groups are stripped from the RDX molecule. The other decomposition species identified below the melting point were CO at amu 28, CH<sub>2</sub>O and NO at 30, C<sub>2</sub>H<sub>4</sub>N at 42, N<sub>2</sub>O at 44, NO<sub>2</sub> at 46, and C<sub>2</sub>H<sub>4</sub>N<sub>2</sub> at 56. Incomplete stripping of the ring resulted in a peak at 128 as intense as those at 82 and 83. This may be caused by the removal from the RDX ring of two NO<sub>2</sub> molecules and an H<sub>2</sub> molecule, leaving

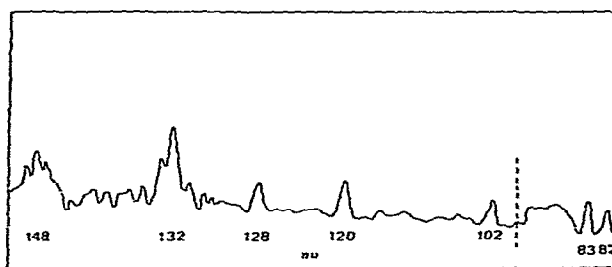
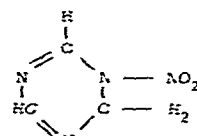
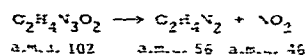
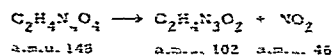


Fig. 3. Decomposition of RDX above the melting point at 220°C; amu range 82–148; mass spectrometric peaks correspond to: 82 = C<sub>3</sub>N<sub>3</sub>H<sub>4</sub>, 83 = C<sub>3</sub>N<sub>3</sub>H<sub>5</sub>, 102 = C<sub>2</sub>H<sub>4</sub>N<sub>3</sub>O<sub>2</sub>, 120 = CH<sub>2</sub>N<sub>3</sub>O<sub>4</sub>, 128 = C<sub>3</sub>H<sub>4</sub>N<sub>4</sub>O<sub>2</sub>, 132 = C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>O<sub>3</sub> and 148 = C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>O<sub>4</sub>.



Further decomposition of the 148 amu species results in release of NO<sub>2</sub> molecules, as



The removal of an O atom results in the amu 132 species, C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>O<sub>3</sub>. The CH<sub>2</sub>N<sub>3</sub>O<sub>4</sub> peak at 120 may be the result of further disintegration of the 148 fragment. This appears to confirm the postulate of Stals [9] that the RDX ring undergoes contraction to the 148 amu species, which releases CH<sub>2</sub>N, and finally results in a molecule at amu 120.

In summary, it may be concluded that the RDX molecule does not appear in the vapor phase; instead, it breaks into at least two large fragments. These fragments, which are unstable, then undergo further decomposition to numerous stable species with relatively low mass values. However, ring stripping of the RDX molecule also occurs, forming dihydro-sym-triazine.

#### Acknowledgement

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