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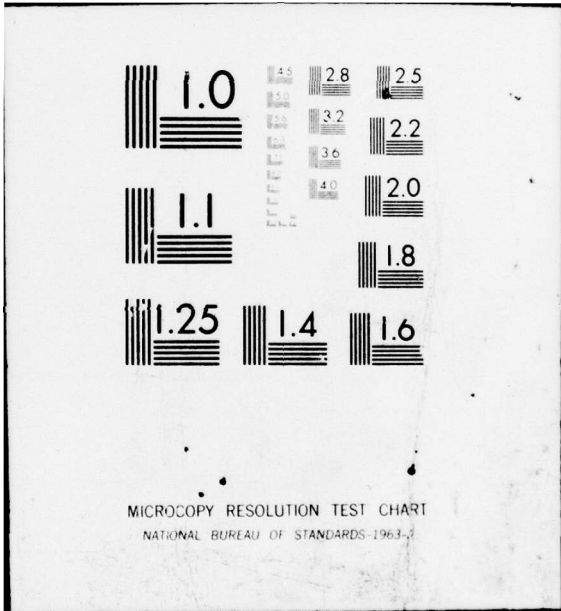
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A MASS-SPECTROMETRIC INVESTIGATION OF THE DECOMPOSITION PRODUCTS OF ADVANCED PROPELLANTS AND EXPLOSIVES.

⑩ Milton Farber and R. D. Srivastava

⑨ ANNUAL SUMMARY REPORT.

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Department of the Navy
Office of Naval Research
Arlington, Virginia 22217

⑮
Contract N00014-75-C-0986

⑪ August 1979

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APPENDIX I.

Mass Spectrometric Investigation of the Thermal
Decomposition of RDX

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I. INTRODUCTION

This Annual Summary Report for the period ending July 31, 1979 presents results of the mass spectrometric investigation of the ignition of several advanced propellants and the vaporization and thermal decomposition of the TATB and HMX molecules. The investigation included:

1. Thermal decomposition of lead additive chelates and ignition of propellant formulations prepared at the Naval Ordnance Station;^{*}
2. Vacuum sublimation and thermal decomposition of TATB;^{**} and
3. Vacuum sublimation and decomposition of HMX.^{***}

Modified Knudsen effusion and Langmuir evaporation experiments were performed employing the specially designed and constructed dual vacuum chamber mass spectrometer system.

Propellant compositions containing the additive, lead chelate of Uvinul 400, produced some methyl radicals in addition to low and intermediate range species, as well as high mass range Pb, PbO and PbNO₂. The ignition products of N-5 propellants were determined. Also, results were obtained on the thermal decomposition of chrysazin and alizarin lead chelates.

The unusual crystallographic structure of the TATB molecule with its extremely large C-C bond lengths and inter- and intramolecular hydrogen bonding results in considerable thermal decomposition as well as its molecular evaporation. The effusion and Langmuir mass spectrometer studies in the temperature range 200 to 300 C showed that TATB both sublimed and decomposed. The effusion experiments showed ring fragmentation as well as the rupturing of the single bonds of the ring constituents. Decomposition produced radical fragments due to the structure of the molecule, which included double bond resonance within the ring and also to the ring constituents.

* Propellant samples obtained from the Naval Ordnance Station, Indian Head, Maryland, Dr. A. T. Camp.

** Propellant samples obtained from Rockwell International, Rocketdyne Division, Dr. Glenn Artz.

*** Propellant samples obtained from the Naval Weapons Center, China Lake, Dr. Thomas Boggs.

During this report period, the HMX evaporation and thermal decomposition effusion-mass spectrometric experiments were completed. Sublimation and decomposition were observed in the temperature range 175 to 275 C. In addition to the observation of the gaseous HMX molecule, the major mode of decomposition was found to be splitting of the molecule into two equal fragments of amu 148. The lower atomic mass molecular and radical fragments were produced by secondary decomposition. An activation energy of 175 kJ/mole (42 kcal/mole) was obtained for the thermal decomposition.

The following sections present details of the experimental apparatus and procedures and a discussion of the results obtained.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

The ignition and thermal decomposition of the advanced propellants were investigated by the effusion-mass spectrometric method. The nitroaromatic and nitramine evaporation and thermal decomposition studies were conducted by both the effusion-mass spectrometric and the Langmuir evaporation-mass spectrometric methods. In effusion experiments the material is placed within an effusion cell having a small orifice (less than 1 mm diameter) which allows the pressure of the gas produced from evaporation or decomposition to be much higher (3 or more orders of magnitude) within the cell than the surrounding vacuum (see Fig. 1). The gas products collide with each other, the cell walls and with the condensed phase many times prior to their effusing from the cell into the mass spectrometer chamber. This may cause secondary decomposition and fragmentation.

The evaporation (Langmuir) method is one in which the material is heated within the main vacuum chamber and allowed to enter the mass spectrometer chamber without further decomposition or collision with other gaseous molecules.

Details of the dual vacuum chamber-quadrupole mass spectrometer system (Fig. 1) used in these experiments have been presented previously.¹ The 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

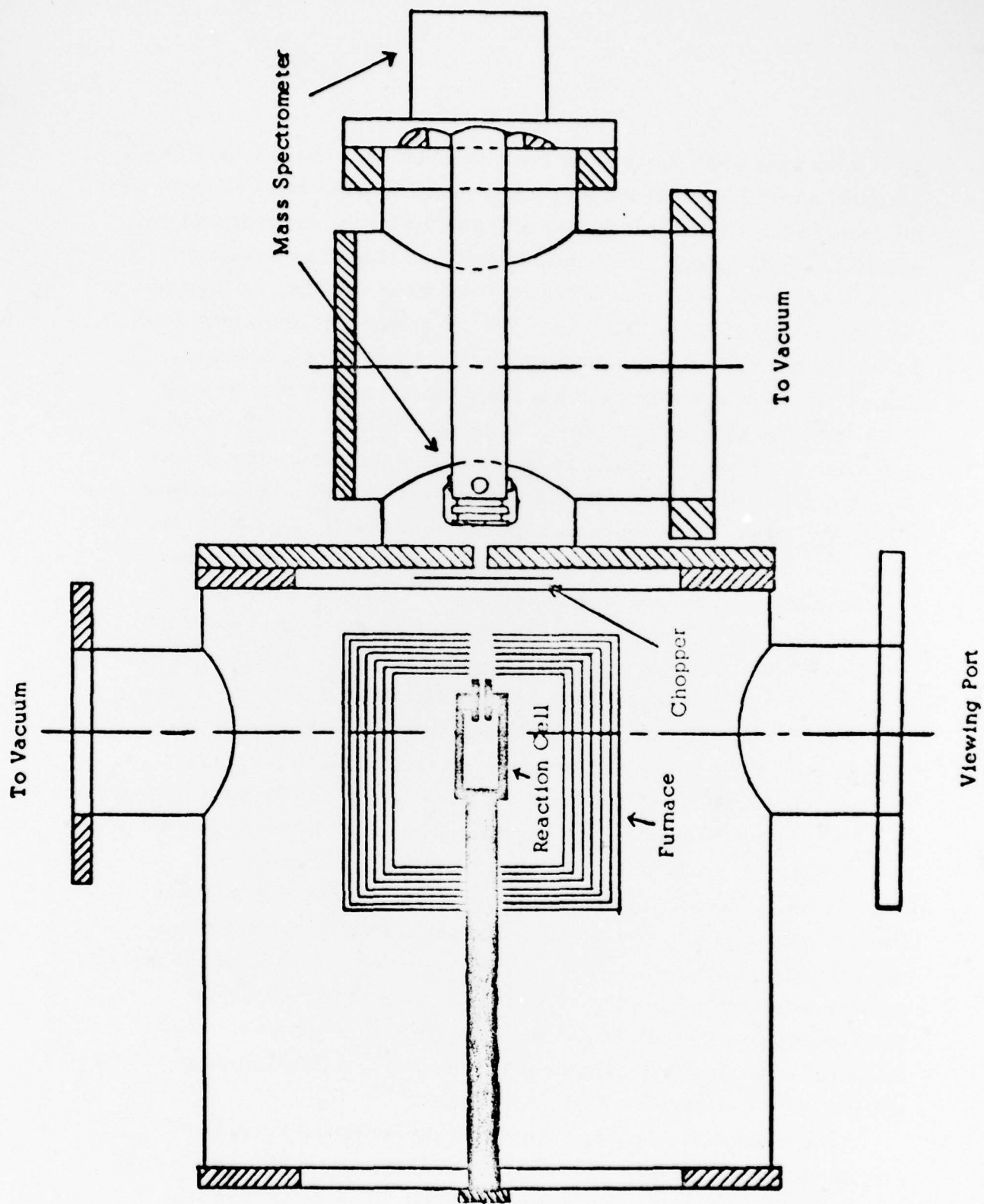


Fig. 1. Dual Vacuum Mass Spectrometer System

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 microseconds. 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.² 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. The concentration of each species is obtained from a knowledge of the cross-sections and other parameters, $n_i \sim I_i T / \sigma_i (E - A_i) S$, where n_i = concentration of species i , I_i = ion intensity for species i , σ = relative cross-section at the maximum of the ionization efficiency curve, A = appearance potential in eV, E = energy of ionizing electrons in eV, S = multiplier efficiency, corrected for molecular beam effects if necessary, and T = absolute temperature. The resolution of the mass spectrometer² is 1 in 500. ^{127}I and $^{254}\text{I}_2$ were employed for amu calibration.

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 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.³⁻⁶

The ionization energies employed were between 14 and 18 eV. Fragmentation of ring constituents requiring the rupture of a single bond by electron impact will occur at lower ionization energies than will fragmentation of the ring itself requiring the rupture of multiple bonds. For example, Figure 2 shows the effect of electron impact ionization

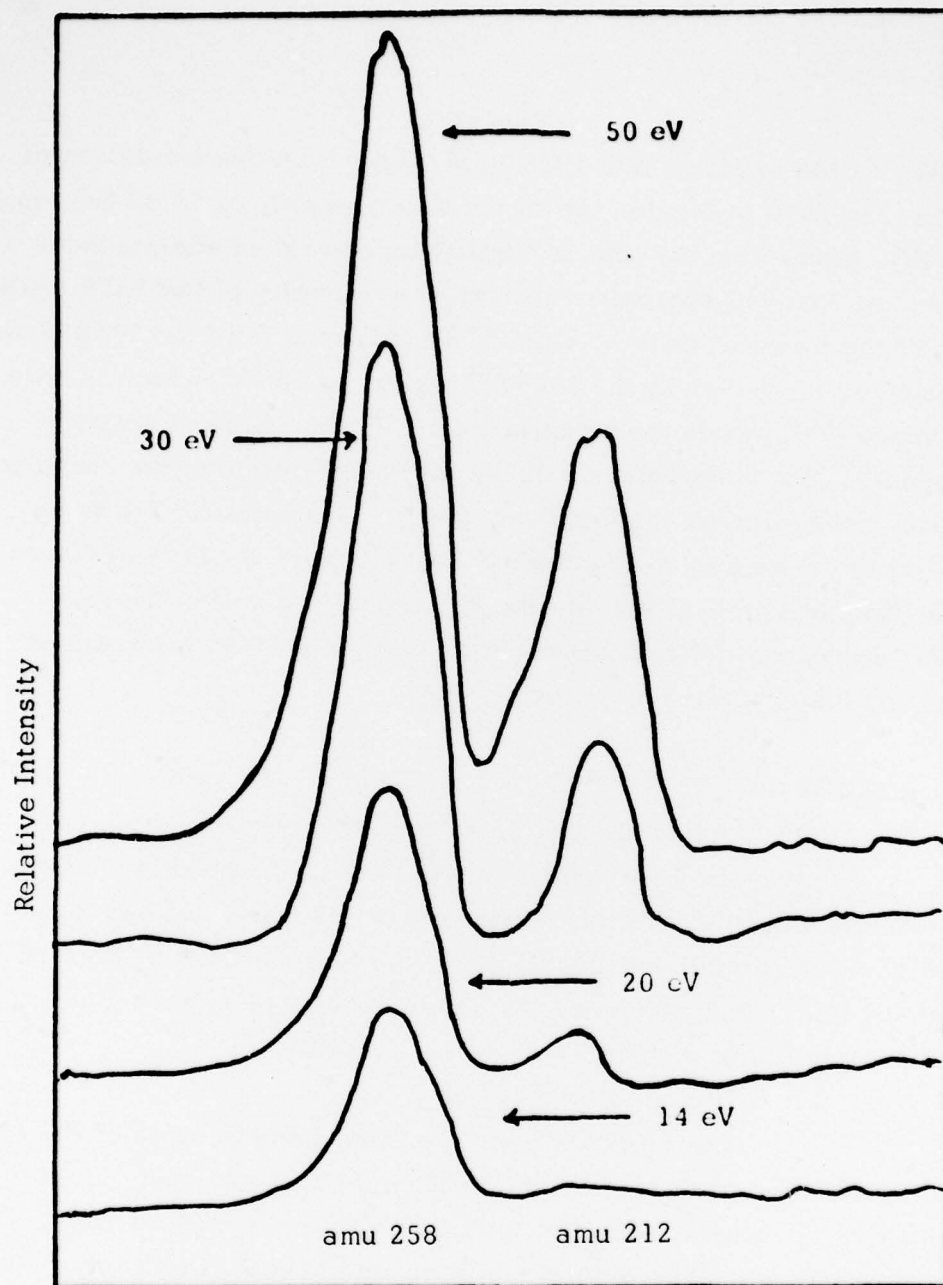


Fig. 2. Electron Impact Fragmentation Pattern of the TATB Molecule. The peak at amu 212 is produced within the ionization chamber of the mass spectrometer with varying relative intensities as a function of the ionizing voltage.

<u>Relative Intensity</u>	<u>Ratio (258/212)</u>
50 eV	2
30 eV	3
20 eV	6
14 eV	>100

energies on the relative intensities and single bond fragmentation of the gaseous TATB molecule. At an ionization energy of 50 eV the removal of an NO_2 group from the ring is readily accomplished and produces a fragment at amu 212 approximately half the intensity of the TATB molecule. At 30 eV the fragment peak at amu 212 is only one-third the TATB peak, and at 20 eV is one-sixth the TATB. Finally, at 14 eV, which is only 2 eV above the appearance potential of TATB, the fragment entirely disappears. The fragmentation of the nitramine ring requires a higher electron impact energy than that required for the removal of a group attached to the ring by a single bond. An example is given in Figure 3, which illustrates the effect of electron impact ionization energies on HMX decomposition products. At an energy of 50 eV a number of peaks are seen, which disappear at 30 eV.

III. RESULTS AND DISCUSSION

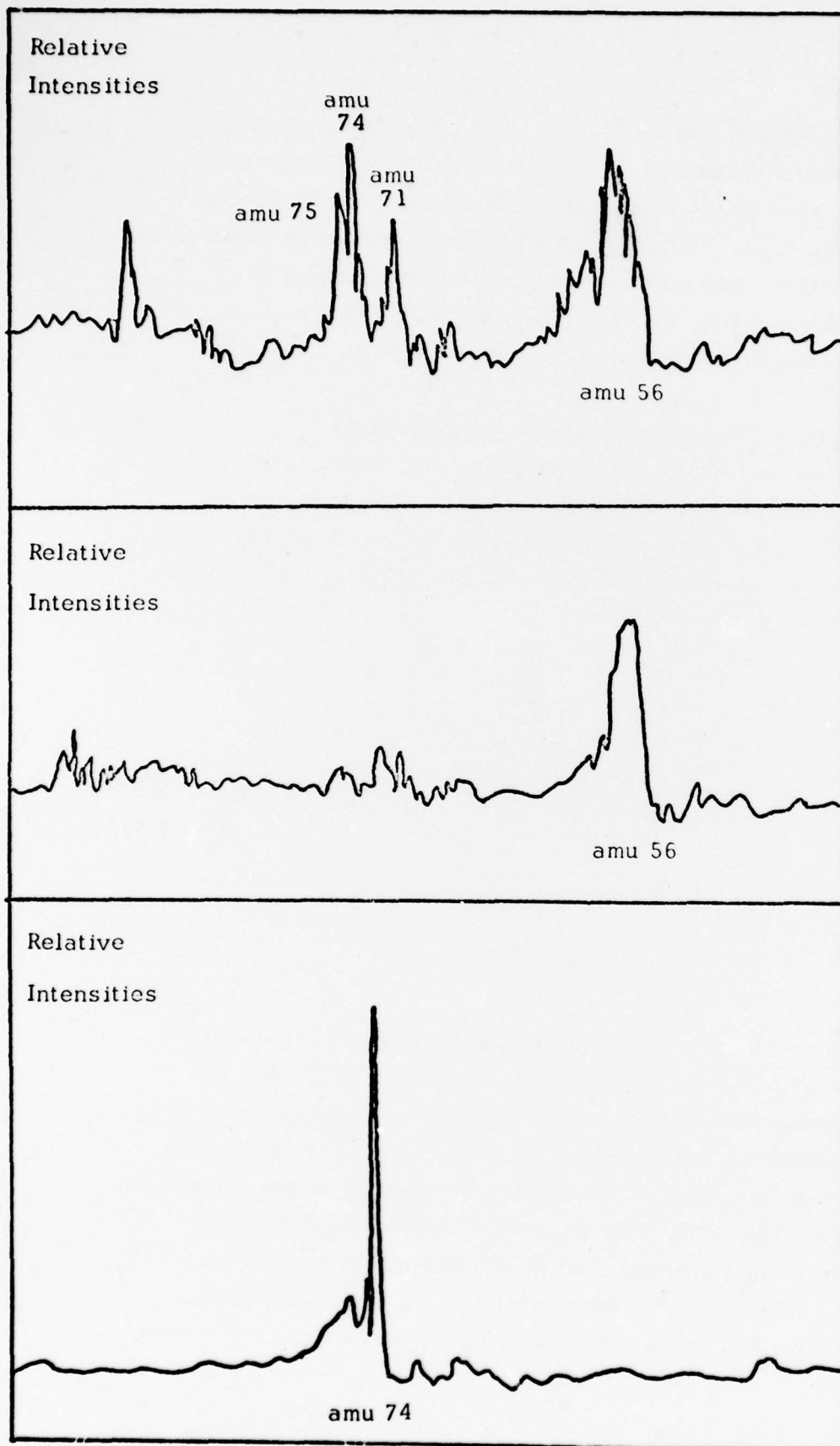
A. Advanced Lead Additive Propellant Compositions

Advanced lead additive propellant compositions prepared at the Naval Ordnance Station, Indian Head, and investigated during this report period included Uvinul 400, which is the lead chelate of 2,4,di-hydroxy benzophenone, the lead chelates of alizarin and chrysazin, and N-5 propellants with and without lead additives.

1. Uvinul 400 Propellant

The previous decomposition investigation of the lead chelate of Uvinul 400 showed this compound to be extremely stable, with no apparent decomposition below 400 C.⁷ During decomposition above 400 C the benzene rings did not break up into smaller fragments, but released volatile species connected to the ring such as carbon monoxide and hydrogen. A quantitative determination of the residue remaining behind showed that it consisted entirely of solid carbon and lead. The gaseous species that evolved upon the decomposition of the molecule above 400 C included H_2 , H_2O and CO , and, at temperatures above 700 C, elemental lead.

The propellant containing the lead chelate of Uvinul 400 (3.5%) consists of the Naval Ordnance Station Matrix No. 1 (93%)



1. PEAKS SEEN AT
50 eV

2. PEAKS SEEN AT
30 eV, amu
range 50 - 65

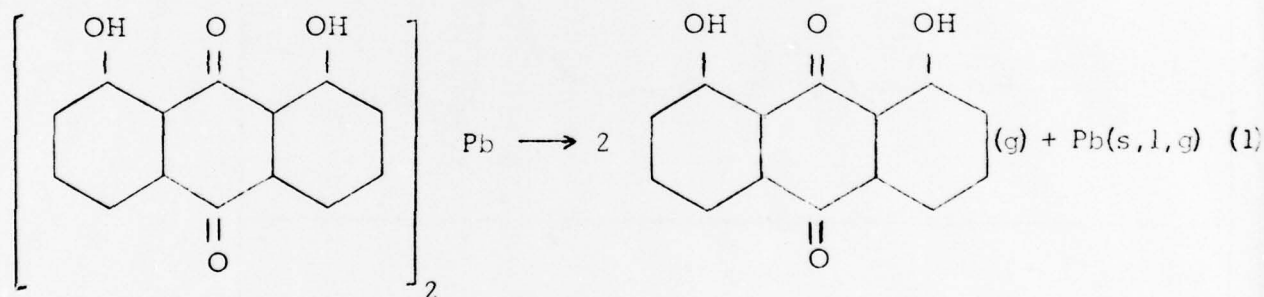
3. PEAKS SEEN
30 eV

Fig. 3. Thermal Decomposition of HMX in Effusion Cell at 225 C

with Carbolac I (0.3%) and MRCBR (3.2%). The components released at ignition are shown in Figure 4. In the low mass number range some CH_3 radicals were seen in the mass spectra in addition to the expected species H_2 , OH and H_2O . The CH_3 radicals did not appear in previous lead additive propellant ignition spectra. Intermediate molecular weight species including CO , NO , O_2 , CO_2 and NO_2 were found. In the high mass range some PbO was observed along with elemental Pb and PbNO_2 .

2. Lead Chelates of Alizarin and Chrysazin

Mass spectrometric investigations were conducted on the thermal decomposition of the lead chelates of alizarin and chrysazin. It was determined that decomposition of the chrysazin chelates results in the vaporization of the organic molecule, with the lead being left behind in the cell.



Only two peaks were identified during the decomposition of this chelate (Figure 5), one at $\text{amu } 240$ at 300 C , and the vaporized Pb atom at 900 C . The molecular weight of the chelate is 687 . A sample weighing 34.3 mg was decomposed at 350 C until no further chrysazin peak was observed in the mass spectrum. The residue weighed 11.0 mg , indicating a 68% weight loss. This is in good agreement with the theoretical value of 70% , assuming elemental lead as the only residue.

Unlike the chrysazin chelate, the lead chelate of alizarin decomposed upon heating without prior vaporization. The thermal

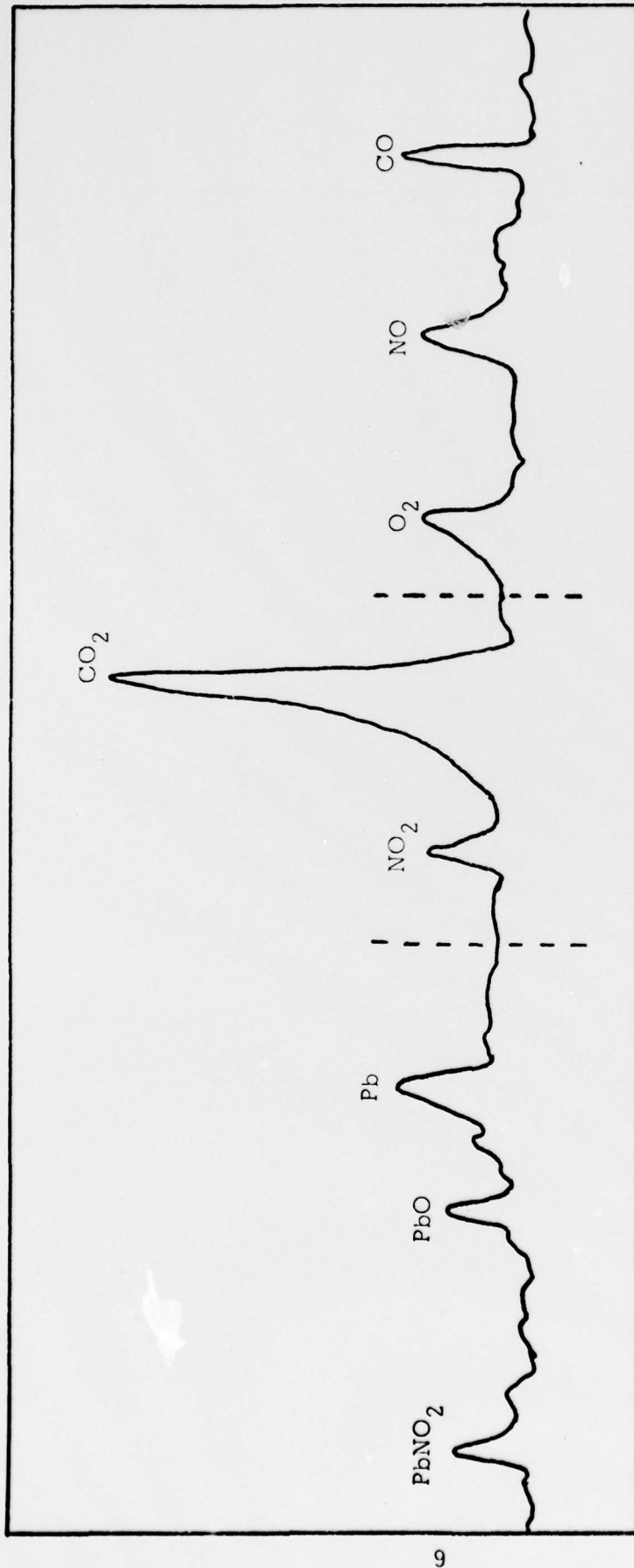


Fig. 4. Ignition Products of Lead Chelate of Uvinul 400 Propellant

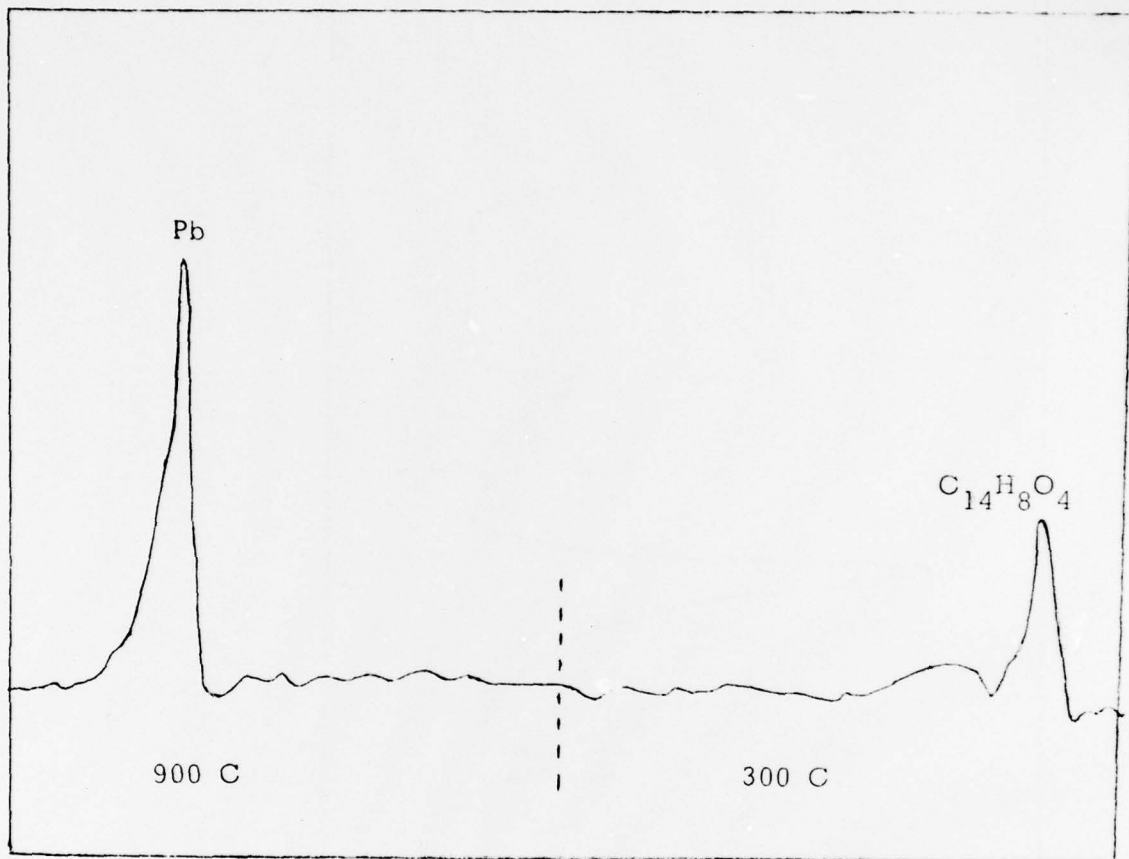
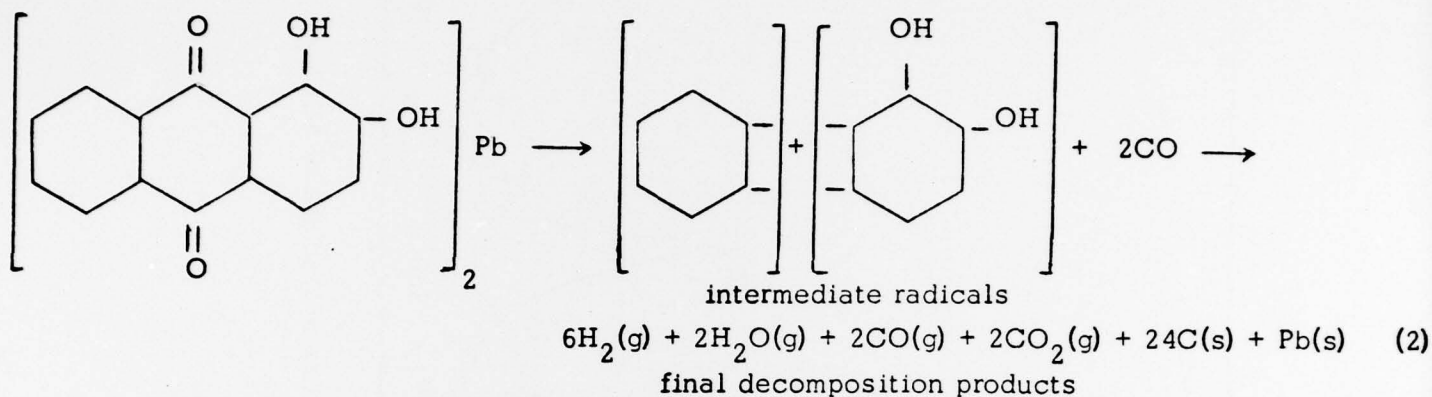


Fig. 5. Mass Spectra of the Thermal Decomposition of the Lead Chelate of Chrysazin

decomposition products are shown in Figure 6. H_2 , H_2O , CO , and CO_2 can be seen at 500 C; at 750 C the Pb atom appears. The chelate decomposition may be postulated as



A sample with an initial mass of 136.6 mg was decomposed at 550 C, with a residual mass of 104.4 mg, indicating that 76% of the chelate did not leave the effusion cell at 550 C. On the assumption that the decomposition path is the breaking of the anthracene structure into two benzene fragments, the theoretical amount of carbon atoms (C_{24}) and Pb which would remain behind would be 73%. Thus the postulation of the decomposition shown by equation (2) is a reasonable one. As a result of the placement of the hydroxy groups the thermal decomposition of the two chelates is completely different. The symmetrical placement of the OH radicals on the outside phenyl rings of the anthraquinone stabilizes the molecule.

3. N-5 Propellants

N-5 propellants with and without lead additives were investigated. In previous work involving mass spectrometric identification of the ignition products,⁸ the species derived from the N-5 propellant were compared to those from JPN, an ordinary double base propellant without lead additives. Figures 7.a., 7.b., and 7.c. depict the low mass range ignition products of JPN, N-5 without lead additives, and N-5 with additives, respectively. The ignition products of the two non-additive propellants are similar, except those of the N-5 propellant include methyl radicals whereas those of the JPN do not.

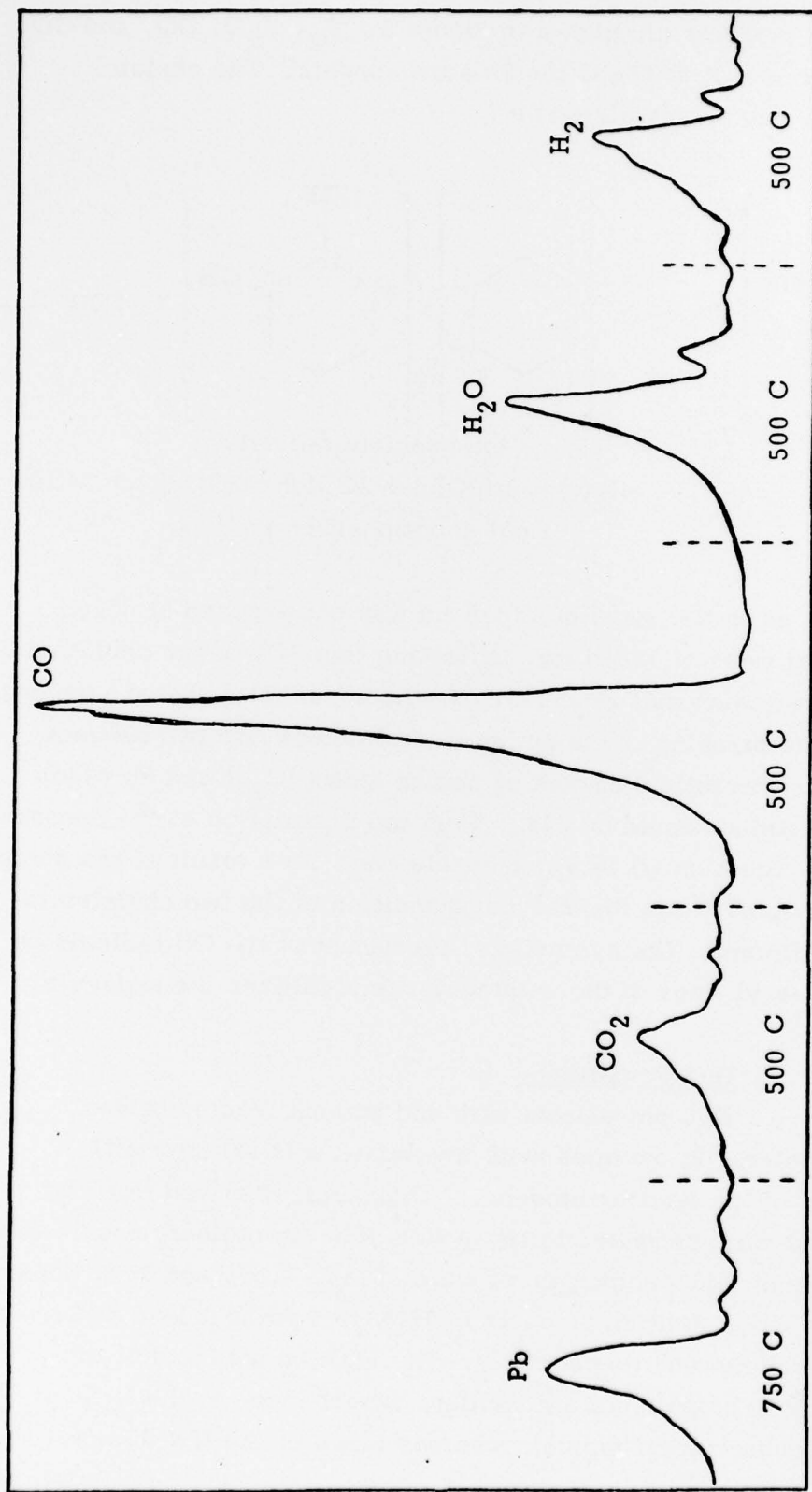


Fig. 6. Mass Spectra of the Thermal Decomposition of the Lead Chelate of Alizarin

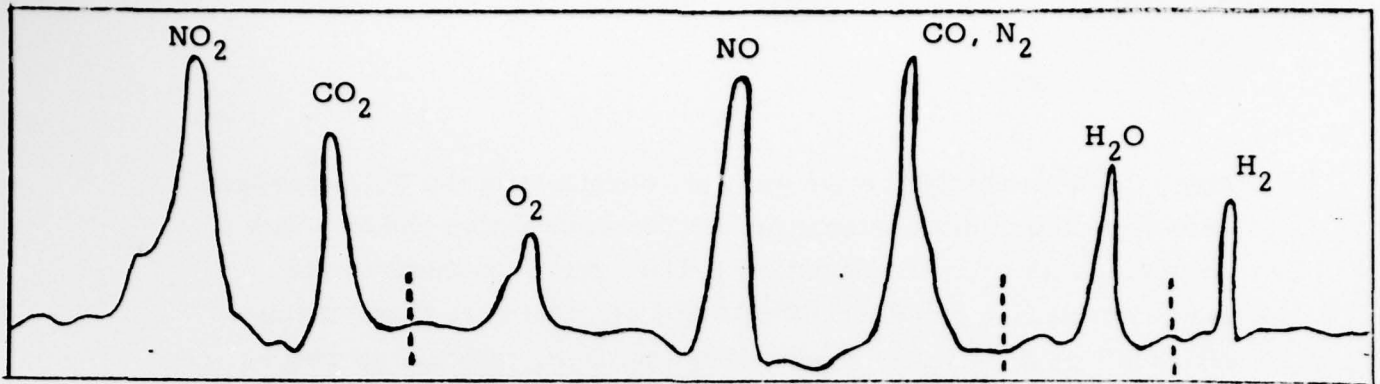


Fig. 7.a. Mass Spectra Resulting from Ignition of JPN Double Base Propellant at 180 C in the 0 to 50 amu Range

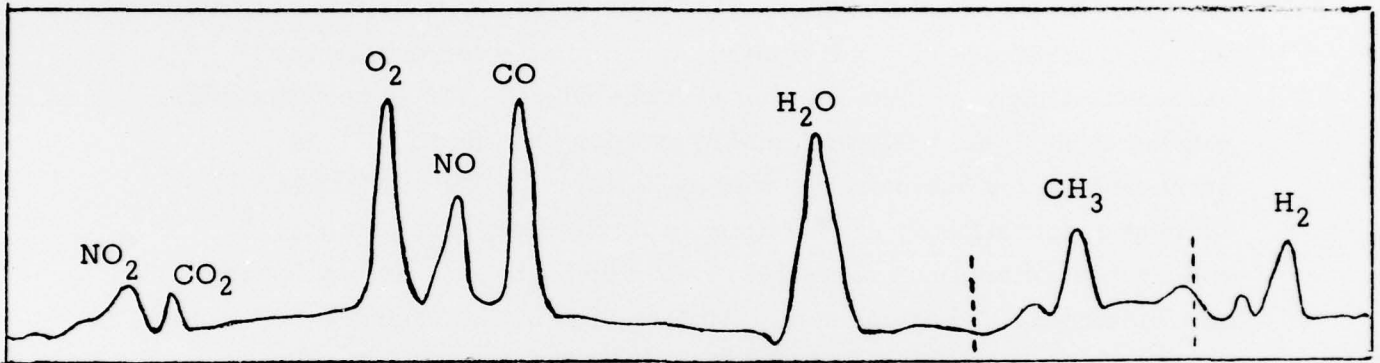


Fig. 7.b. Mass Spectra Resulting from Ignition of N-5 Propellant without Lead Additive in the 0 to 50 amu Range

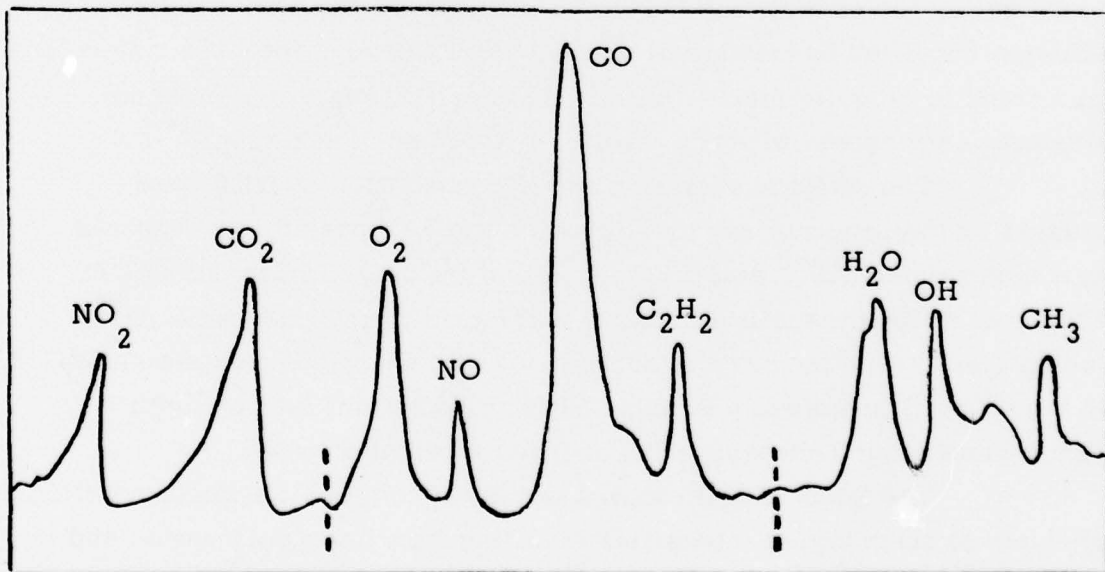


Fig. 7.c. Mass Spectra of N-5 Lead Additive Double Base Propellant Showing Species Released at Ignition in the 15 to 50 amu Range

Also, the NO_2 and CO_2 peaks are more prominent in the JPN propellant. (However, the relative intensities are not quantitative and may vary somewhat with each determination.) The ignition products of the lead additive N-5 propellant (Fig. 7.c.) are similar to those of the non-additive N-5, with the exception that C_2H_2 radicals as well as methyl radicals were observed in the lead additive propellant.

B. Sublimation and Thermal Decomposition of TATB

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) has been described as an unusual molecule.^{9,10} Its structure is quite distortive, with C-C distances of 1.441 Å units, considerably larger than the average C-C bond lengths in other benzene rings.⁹ It has no observable melting point¹⁰ and has considerable hydrogen bonding.^{9,10} Its activation energy has been reported by Bailey¹¹ as 250.6 kJ/mole, its heat of formation as -154.2 kJ/mole by Hardesty and Kennedy,¹² and its heat of sublimation as 168.3 kJ/mole by Shaw¹³ and by Rosen and Dickinson.¹⁴ Vacuum sublimation studies by the Langmuir technique were conducted by Rosen and Dickinson¹⁴ in the temperature range 129.3 to 177.3 C, with vapor pressures of 7.33×10^{-8} and 1.67×10^{-5} mm Hg, respectively.

The sublimation and thermal decomposition of TATB were investigated at this laboratory by two combined mass spectrometric techniques: the evaporation (Langmuir experiment) method, and the effusion (modified Knudsen cell) method. Below 200 C the TATB molecule was found to be quite stable, with little vaporization; vapor pressure measurements agreed with the results of Rosen and Dickinson.¹⁴

The direct evaporation and decomposition of TATB were studied by the Langmuir method, in which the TATB was directly heated in a high vacuum (10^{-8} atm) in the temperature range 200 to 300 C. At 250 C the molecule sublimed readily, with some thermal decomposition taking place. The products of sublimation and decomposition are shown in Figure 8. The molecule at amu 258 is the dominant species, with decomposition products appearing at lower concentrations.

The Knudsen method was employed to study the decomposition products at much higher intensities resulting from beam collimation and

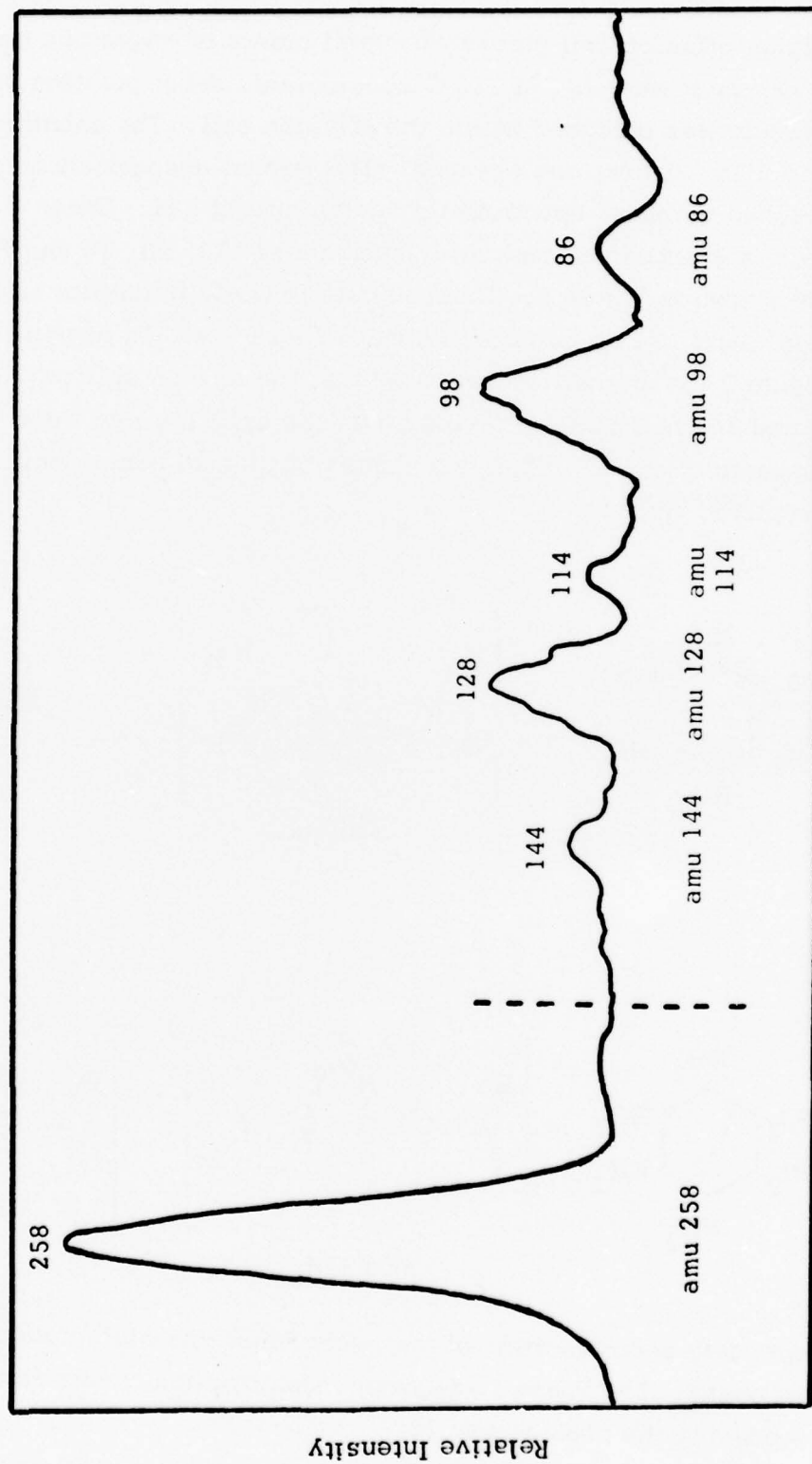
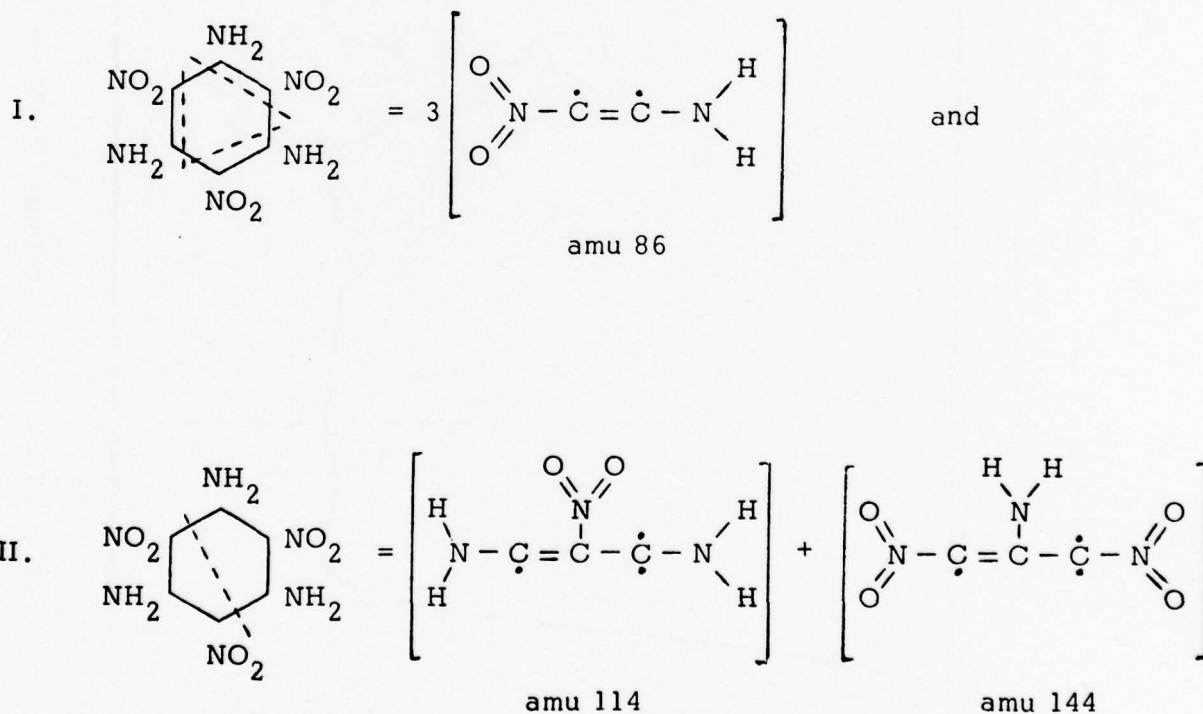


Fig. 8. TATB Evaporation and Decomposition (Langmuir Experiment)

from a higher effusion cell pressure (several orders of magnitude greater than the Langmuir method). At 250 C considerable decomposition of the TATB molecule was produced within the effusion cell. The entire mass range from 1 to 258 amu was scanned. The largest decomposition product which reached the mass spectrometer had an amu of 144. Other large fragments appeared, with mass numbers of 114, 98, 86 and 70. These are shown in Figure 9. The molecule initially fragments into three equal parts or into two unequal mass fragments. An examination of the Figure 9 ion intensities indicated that the uneven splitting into amu 114 and 144 fragments is favored over the splitting into three even fragments of amu 86. The two phases of thermal decomposition may be depicted as:



Secondary decomposition of the major fragments also produced prominent peaks. The Phase I. decomposition fragment loses an amine group, producing the peak at amu 70,

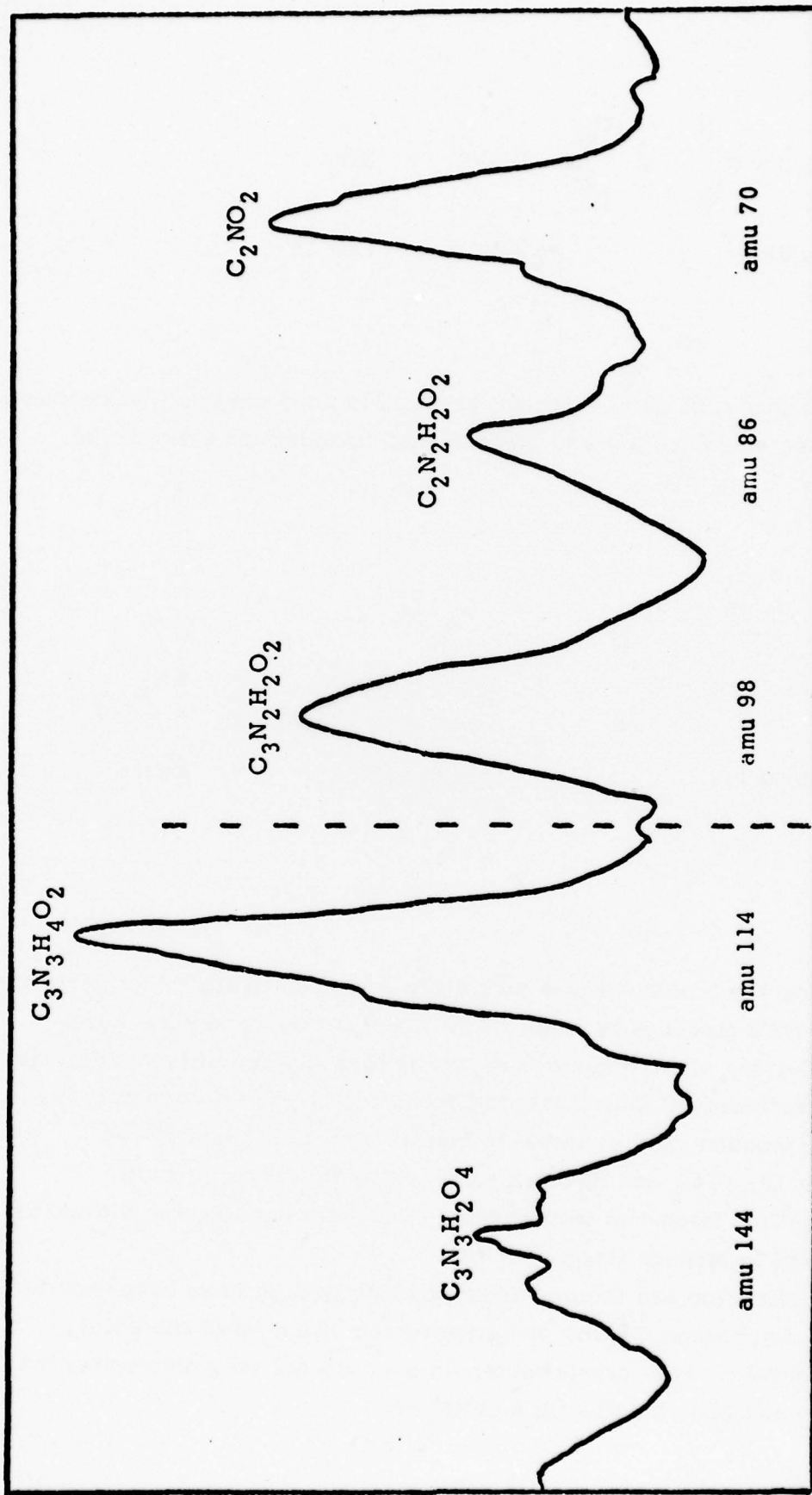
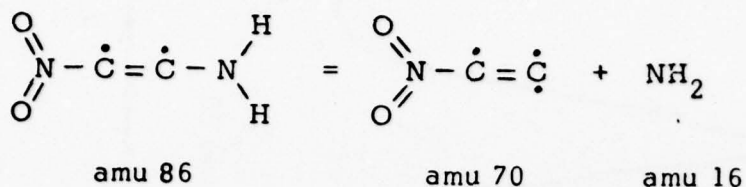
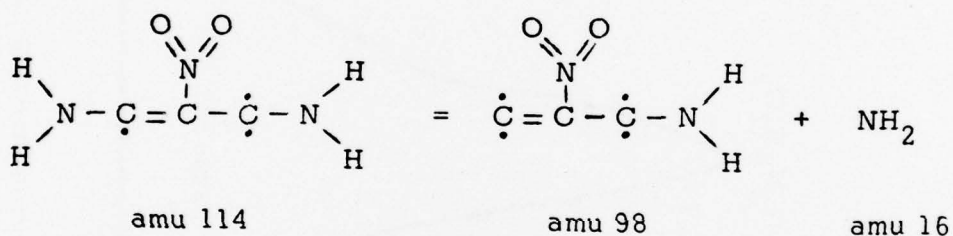


Fig. 9. Primary Thermal Decomposition Products of TATB at 230 C



The Phase II. large fragment at amu 114 undergoes further decomposition, also losing an amine group to produce the prominent peak at amu 98,



From the studies at this laboratory it appears certain that decomposition of solid TATB produces radicals. The radicals may or may not have long half-lives since they are sampled in less than a millisecond by the mass spectrometer. Continued collisions within the effusion cell probably produce smaller stable fragments, such as those shown in Figure 10. CO_2 and H_2O are produced by the larger primary decomposition fragments which, through numerous collisions within the cell, react to produce these species.

Sublimation and thermal decomposition results have been reported by Cady and Larson,¹⁰ who investigated the structure of the solid TATB molecule. From crystallographic experiments they determined the structure and bond lengths (in Å units) as

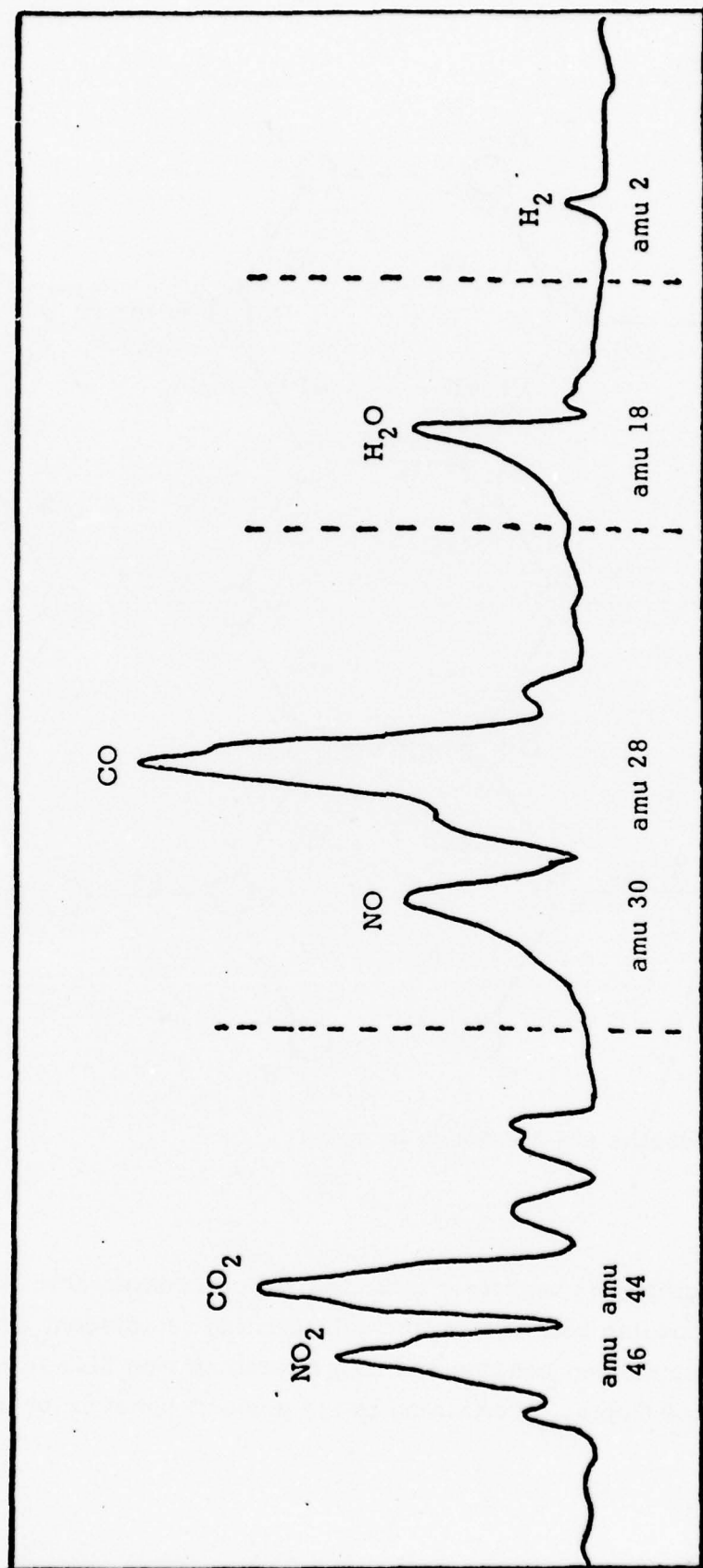
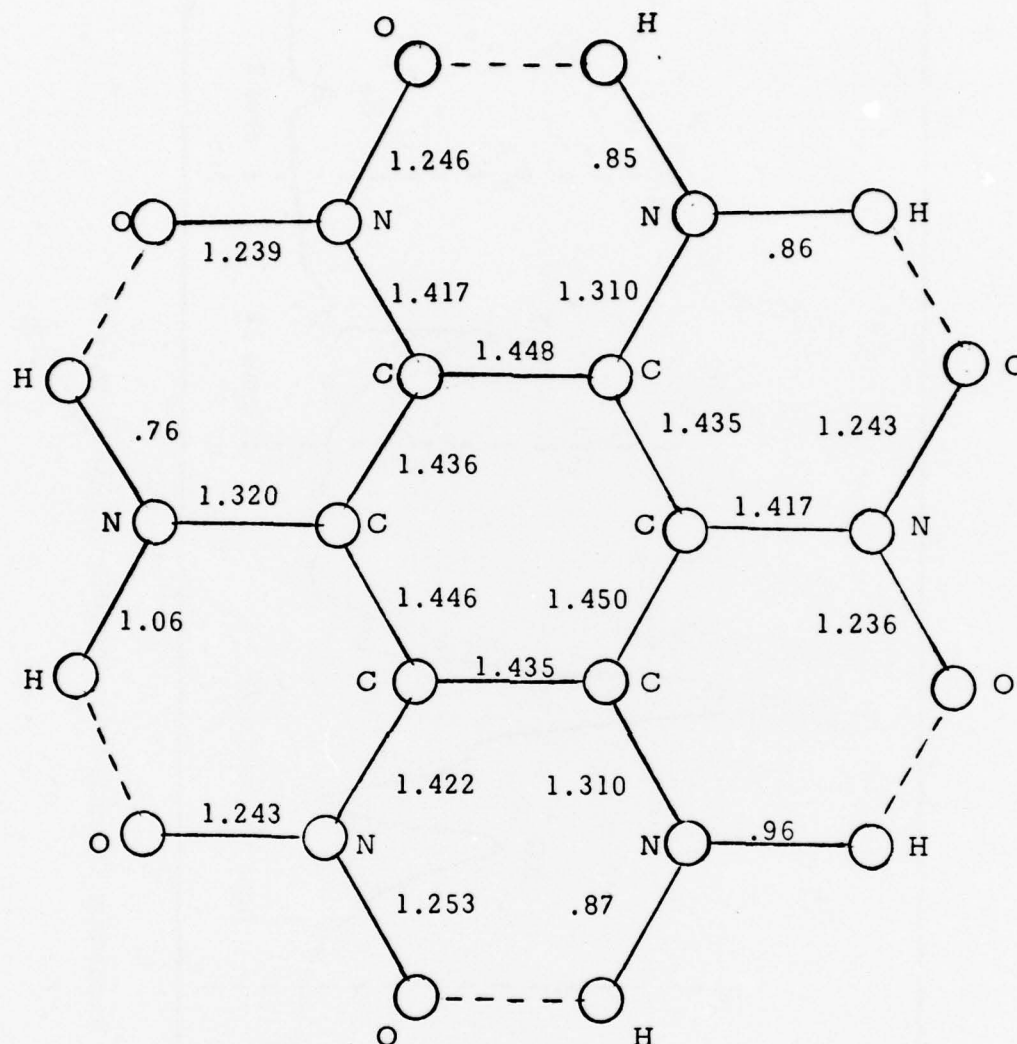


Fig. 10. Secondary Thermal Decomposition Products of TATB



Note: Bond lengths are not drawn to scale.

The bond lengths are completely distorted with a considerable amount of hydrogen bonding both within the molecule and to adjacent molecules. Considerable hydrogen bonding and ring stretching was also reported by Deopura and Gupta.⁹ Pertaining to the unusual behavior of the

molecule, Cady and Larson¹⁰ commented that the molecule contained extremely long C-C bonds in the benzene ring, very short C-N bonds, and 6 bifurcated hydrogen bonds. Thermal decomposition would be expected as a result of the stretched bonds in the unusual structure, as determined in the mass spectrometer studies at this laboratory and by other investigators.

Britt and Moniz¹⁵ have studied, by means of electron spin resonance, the formation of free radicals resulting from the irradiation by ultraviolet of TATB. They recently reported that a considerable concentration of unknown free radicals was observed by means of ESR of the thermal decomposition of TATB at a temperature of 350 C and at a pressure of 1 atm.¹⁶ The free radicals identified mass spectrometrically at this laboratory were obtained at somewhat lower temperatures and at pressures less than 10^{-4} atm.

C. Sublimation and Thermal Decomposition of HMX

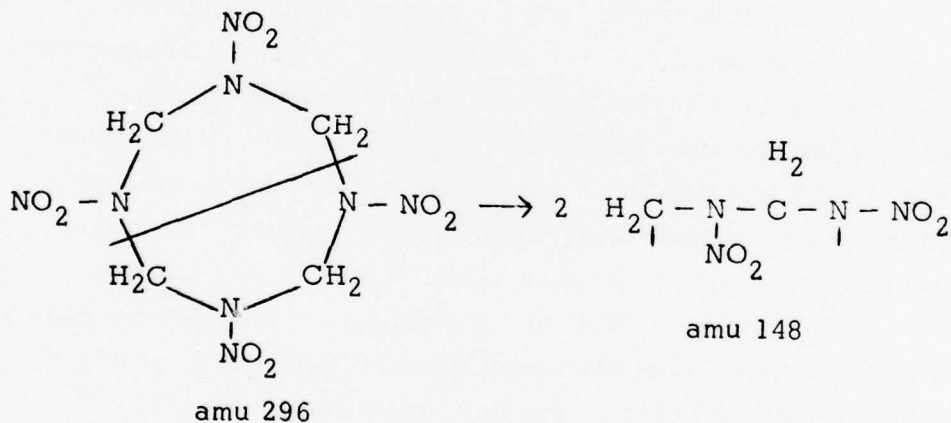
During this report period the evaporation and thermal decomposition studies of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) employing the effusion cell technique described in the Experimental Section were completed. The β form of HMX, which is stable at room temperature,¹⁷ was used in all experiments and is referred to as HMX in this report. The results obtained, including activation energies and probable modes of decomposition, are presented in this section. Probable mechanisms of HMX evaporation and decomposition will be discussed upon completion of the final phase of the studies employing the Langmuir evaporation technique.

The results from fairly low temperature effusion cell measurements by Rosen and Dickinson¹⁴ and by Crookes and Taylor¹⁸ indicate that HMX evaporates without appreciable decomposition. Rosen and Dickinson reported a vapor pressure range of 10^{-11} to 10^{-10} atm in the temperature range 98 to 130 C for HMX, and Crookes and Taylor determined vapor pressure data varying from 10^{-7} to 10^{-5} atm in the temperature range 188 to 213 C. Our effusion experiments were performed

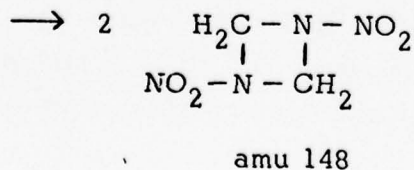
in the range 175 to 275 C, with cell evaporation and decomposition pressures varying from 5×10^{-7} to 5×10^{-3} atm.

Between 175 and 200 C the evaporation of HMX was predominant. Figure 11 shows the relative intensity of HMX at 200 C, with a smaller relative concentration appearing at amu 222. As the temperature approached 225 C considerable decomposition occurred (Figure 12). Relative concentrations at amu 148, 128, 120 and 102 are also depicted. The relative concentration of the peaks at amu 74 and 56 at 225 C are shown in Figure 13. The peaks appearing in the low amu 18 to 46 range are depicted in Figure 14.

The apparent primary mode of HMX decomposition is ring splitting, as



or possible joining of the split C and N bonds resulting in



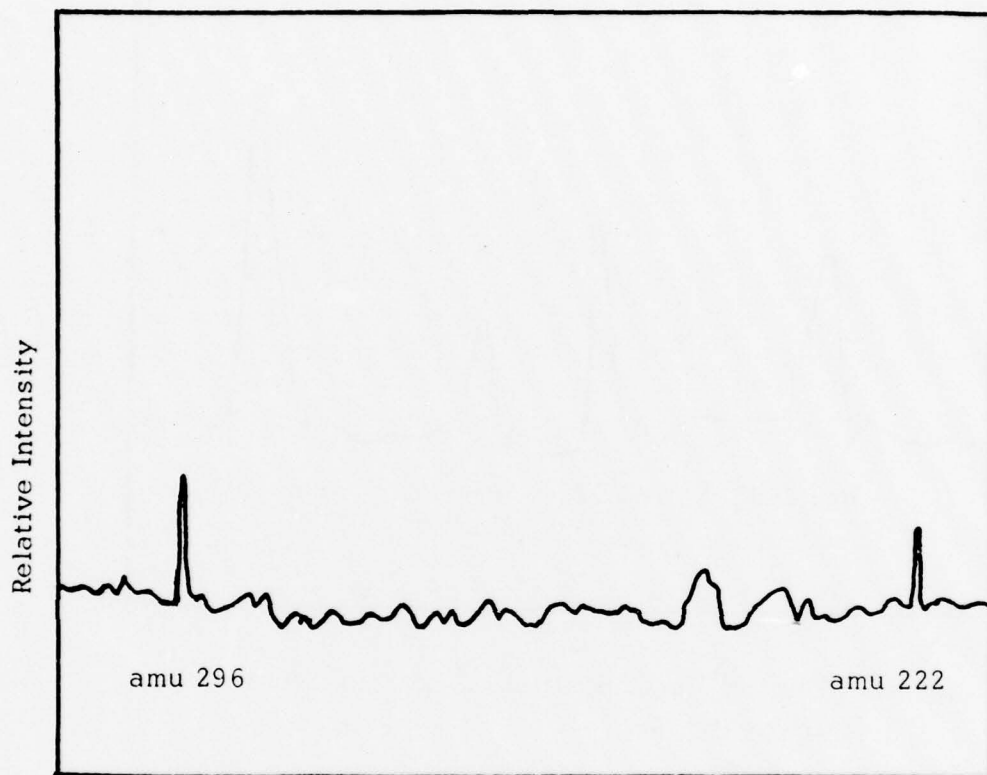


Fig. 11. Evaporation and Thermal Decomposition of HMX in Effusion Cell at 200 C

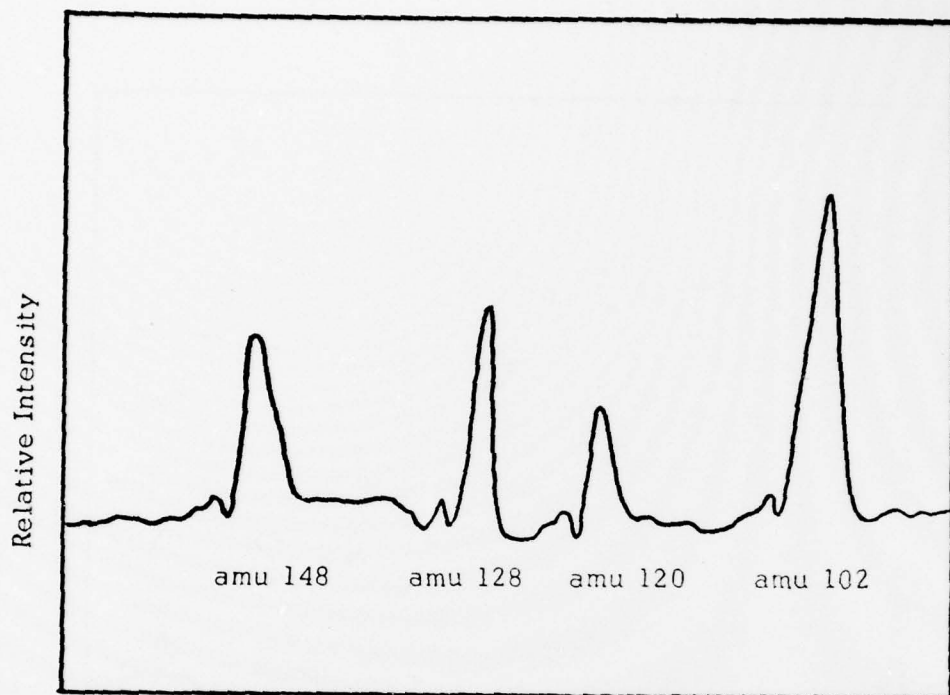


Fig. 12. Thermal Decomposition of HMX in Effusion Cell
at 225 C

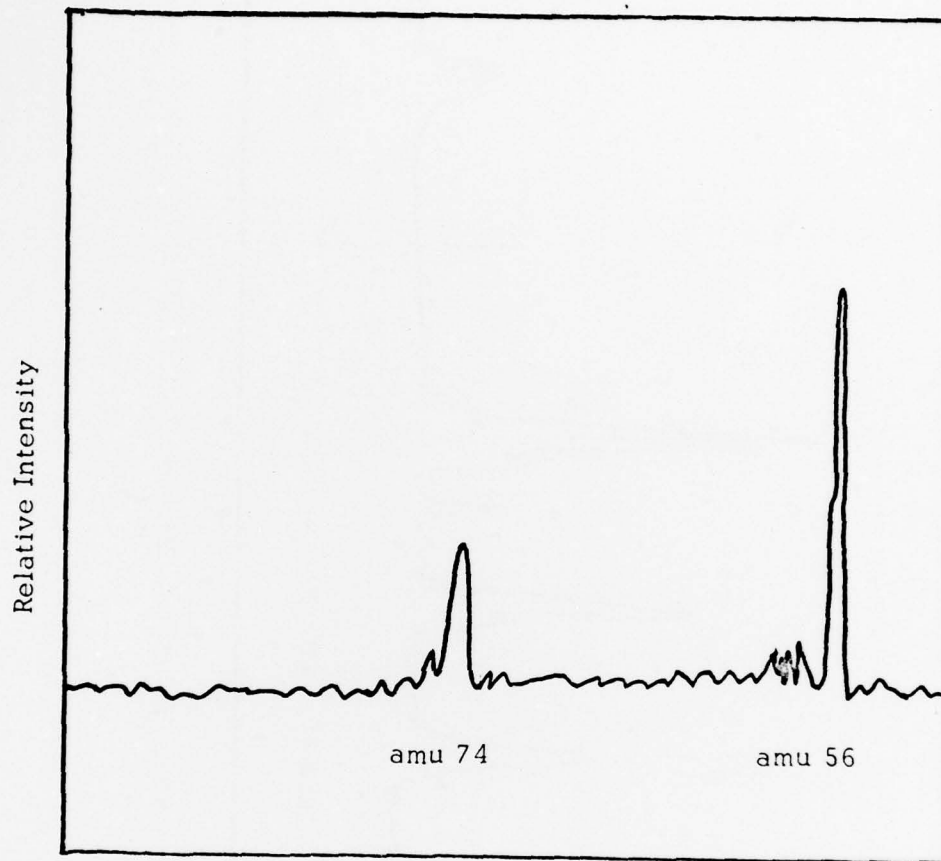


Fig. 13. Thermal Decomposition of HMX in Effusion Cell at 225 C

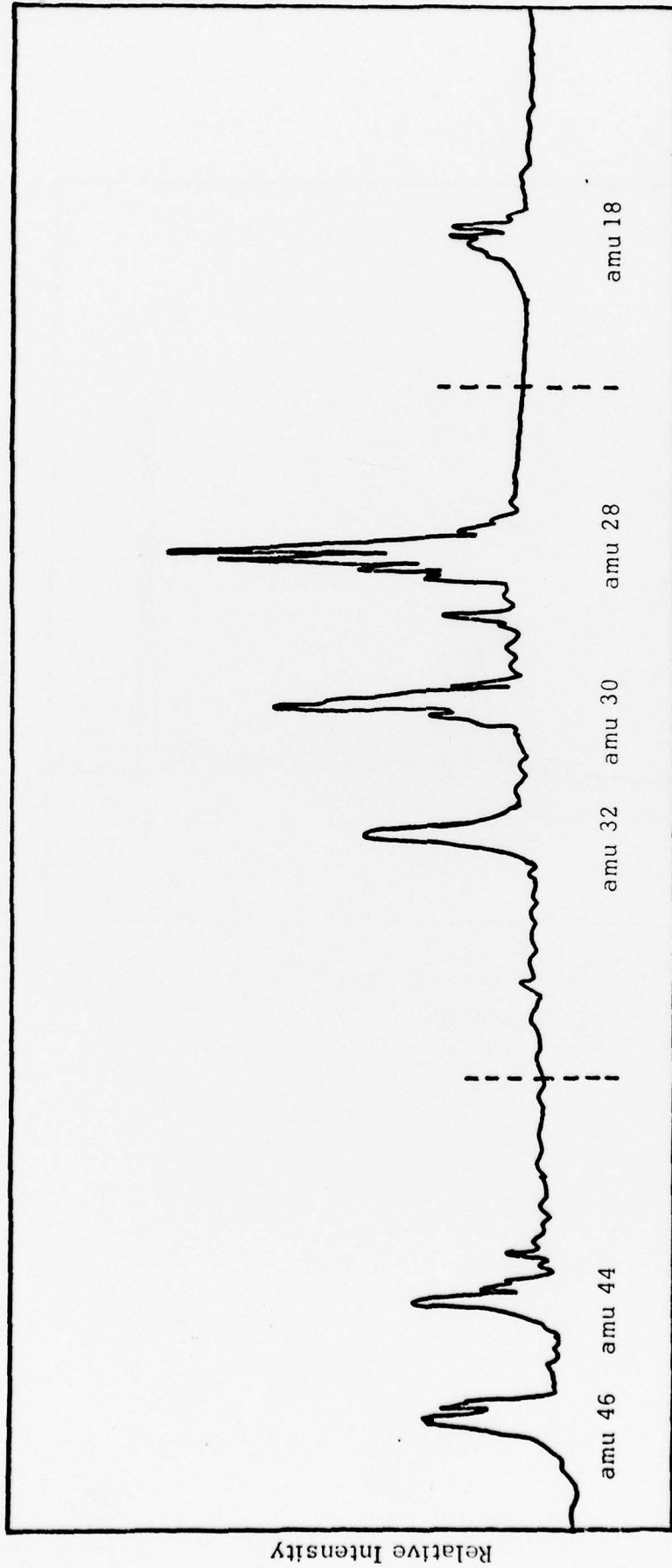
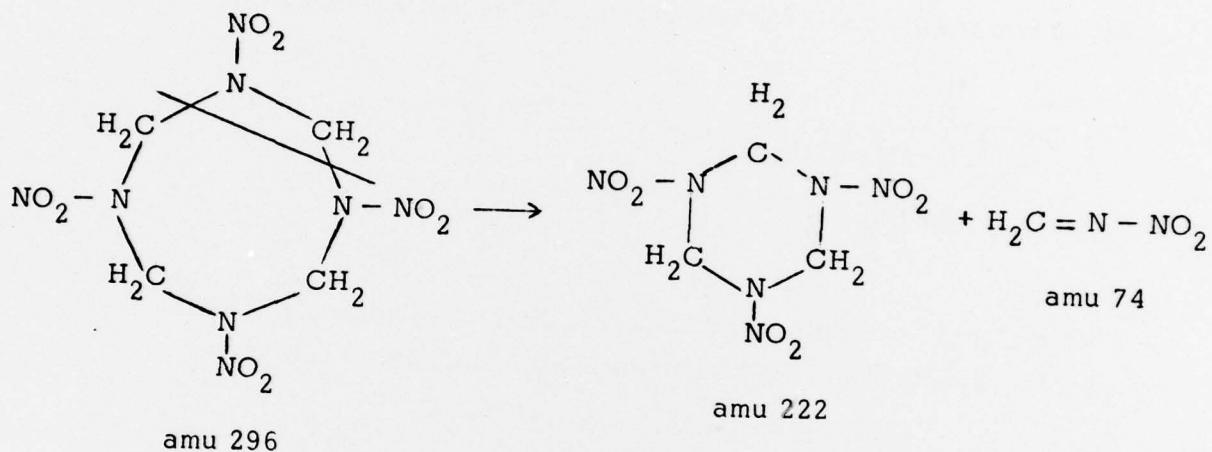


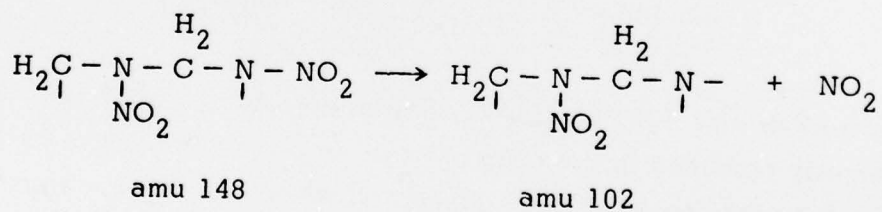
Fig. 14. Thermal Decomposition of HMX in Effusion Cell at 225 C

Apparently N-NO₂ bond splitting is not a primary mode of decomposition, since the amu 250 fragment was not observed in these and other studies.¹⁹

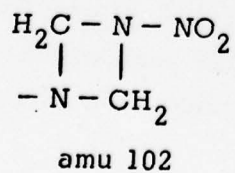
Another mode of decomposition is



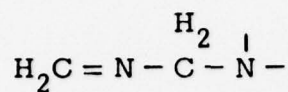
Further decomposition may occur as



or with bond closure resulting in

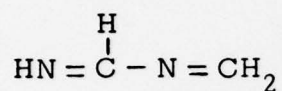


The 102 fragment splits off another NO₂ group, yielding



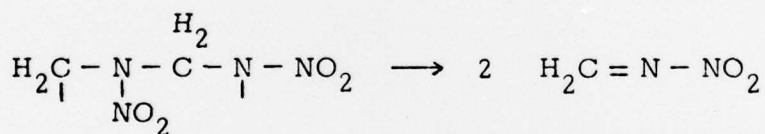
amu 56

which can rearrange to form a more stable resonating molecule,



amu 56

This molecule can split to produce two H₂C = N• radicals. The amu 148 fragment can also split into two equal stable molecules,



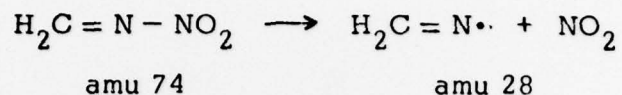
amu 148

amu 74

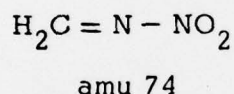
The peaks at amu 120, CH₂N₃O₄, and at amu 128, C₃H₂N₄O₂, are apparently produced in the effusion cell as a result of the reaction of the gas with the condensed phase and with each other. These peaks have also been observed by Goshgarian,¹⁹ Stals,²⁰ and Suryanarayana, et al.²¹

Beyer²² in ESR studies found considerable free radicals produced from the decomposition of HMX at 260 C. He attributed this free radical spin resonance to the formation of H₂CN• at amu 28. Figure 14 shows a high concentration of the amu 28 peak which, in all probability, is a mixture of the decomposition products CO, N₂, and H₂CN.

Beyer²² postulated that the radical, H₂CN, is derived from



Our studies yielded an activation energy of 175 kJ/mole (42 kcal/mole) for the decomposition to NO₂ groups, as shown in Figure 15. Goshgarian¹⁹ reported activation energies of 159 ± 8 kJ/mole (38 ± 2 kcal/mole) from 250 to 270 C and 175 ± 8 kJ/mole (42 ± 2 kcal/mole) from 271 to 280 C. McGuire²³ reported an Ea of 175 kJ/mole (42 kcal/mole) from the decomposition of HMX to



The enthalpy of sublimation obtained by Taylor and Crookes¹⁸ was 163 kJ/mole (39 kcal/mole).

IV. PUBLICATIONS AND MEETING PRESENTATIONS

The following publication appeared during this report period, and is included as Appendix I:

Milton Farber and R. D. Srivastava, "Mass Spectrometric Investigation of the Thermal Decomposition of RDX," *Chemical Physics Letters*, Vol. 64, p. 307 (1979).

A paper entitled "Mass-Spectrometric Investigation of the Chemistry of Advanced Composite and Double Base Propellants" was presented at the 15th JANNAF Combustion Meeting held at the Naval Underwater Systems Center, Newport, Rhode Island in September 1978, and published in Volume II of the Proceedings (CPIA Publication 298, February 1979, p. 423).

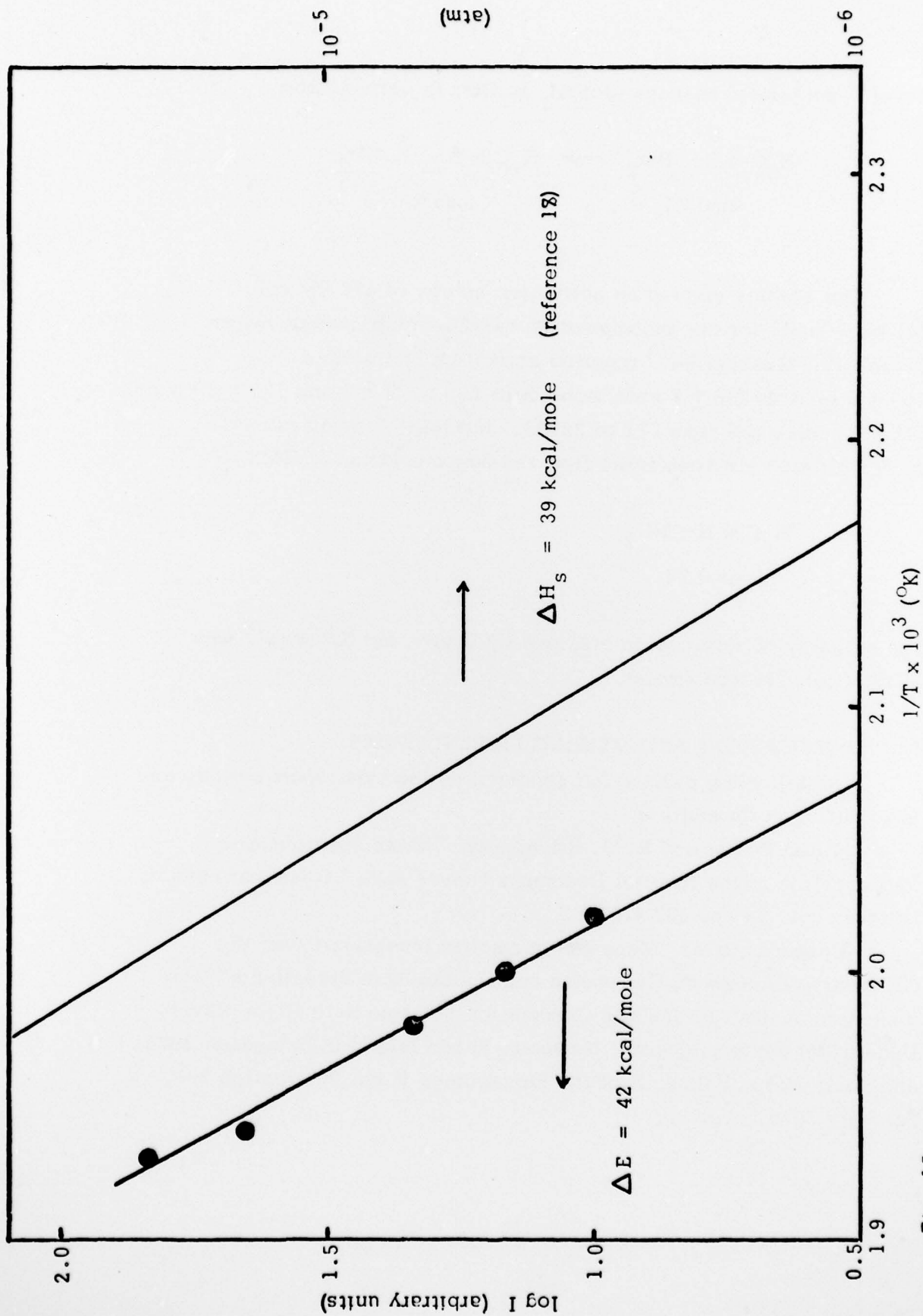


Fig. 15. TEMPERATURE DEPENDENCE OF NO_2 FROM THE THERMAL DECOMPOSITION OF HMX IN AN EFFUSION CELL. THE RESULTS OF TAYLOR AND CROOKES ARE FROM A KNUDSEN WEIGHT LOSS EXPERIMENT ASSUMING HMX AS THE ONLY PRODUCT.

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APPENDIX I

Volume 64, number 2

CHEMICAL PHYSICS LETTERS

1 July 1977

MASS SPECTROMETRIC INVESTIGATION OF THE THERMAL DECOMPOSITION OF RDX

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Received 23 February 1979

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_2 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_2O , H_2 , CO , CH_2O and CO_2 . 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_2O and CH_2O . No NO_2 was observed. Rauch and Fanelli [2], who conducted studies between 207 and 227°C, above the melting point, reportedly observed NO_2 and a number of other gaseous products, including N_2O , NO , CH_2O , CO , CO_2 , H_2O and HCN . Goshgarian [3] also observed NO_2 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_3 and CH_2O_2 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.

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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 μ 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,

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

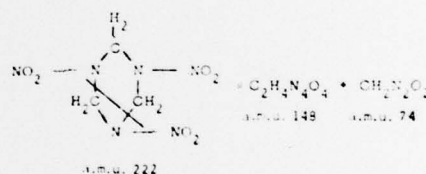
where n_i is the concentration of species i , I_i the ion intensity for species i , σ the relative cross section at the maximum of the ionization efficiency curve, A_i the appearance potential in eV, E the energy of ionizing electrons in eV, S the multiplier efficiency, corrected for molecular beam effects 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

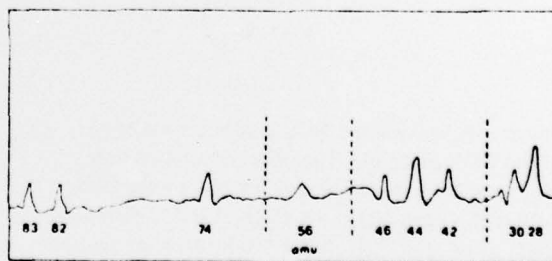


Fig. 1. Decomposition of RDX below the melting point at 200°C; amu range 28-83; mass spectrometric peaks correspond to: 28 = CO, 30 = CH_2O and NO, 42 = $\text{C}_2\text{H}_4\text{N}$, 44 = N_2O , 46 = NO_2 , 56 = $\text{C}_2\text{H}_4\text{N}_2$, 74 = $\text{CH}_2\text{N}_2\text{O}_2$, 82 = $\text{C}_3\text{N}_3\text{H}_4$ and 83 = $\text{C}_3\text{N}_3\text{H}_5$.

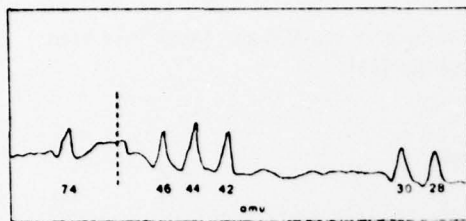
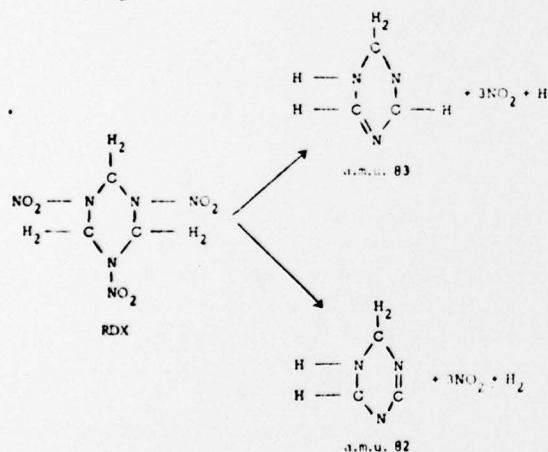


Fig. 2. Decomposition of RDX above the melting point at 220°C; amu range 28–74; mass spectrometric peaks correspond to: 28 = CO, 30 = CH₂O, 42 = C₂H₄N, 44 = N₂O, 46 = NO₂ and 74 = CH₂N₂O₂.

stable molecule, CH₂N₂O₂. 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 NO₂ 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 NO₂ groups:



In this decomposition the NO₂ groups are stripped from the RDX molecule. The other decomposition species identified below the melting point were CO at amu 28, CH₂O and NO at 30, C₂H₄N at 42, N₂O at 44, NO₂ at 46, and C₂H₄N₂ 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 NO₂ molecules and an H₂ molecule, leaving

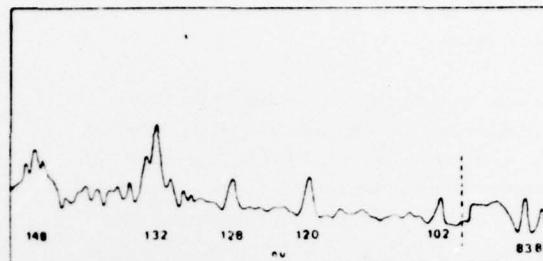
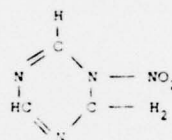
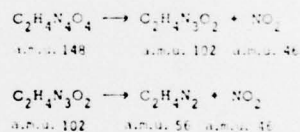


Fig. 3. Decomposition of RDX above the melting point at 220°C; amu range 82–148; mass spectrometric peaks correspond to: 82 = C₃N₃H₄, 83 = C₃N₃H₅, 102 = C₂H₄N₃O₂, 120 = CH₂N₃O₄, 128 = C₃H₄N₄O₂, 132 = C₂H₄N₄O₃ and 148 = C₂H₄N₄O₄.



Further decomposition of the 148 amu species results in release of NO₂ molecules, as



The removal of an O atom results in the amu 132 species, C₂H₄N₄O₃. The CH₂N₃O₄ 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 CH₂N, 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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		6. PERFORMING ORG. REPORT NUMBER
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The results of a mass spectrometric study of several advanced propellants and explosives to determine the chemistry and kinetics of their decomposition are presented. The technical program involved three propellant groups: (1) ignition and thermal decomposition of advanced lead organic additive propellants; (2) sublimation and thermal decomposition of trinitro-triamino benzene; and (3) sublimation and thermal decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX).		