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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The structure of RDX has been compared by the use of Fourier transform infrared spectroscopy in the gas phase, melt phase, solution phase, and the solid β and α phases. The gas, melt, and solid β-RDX phases have not been studied previously. The RDX molecule has essentially C_{3v} molecular structure in all environments except the stable solid α-RDX phase. The RDX and HMX melts were found to be comprised almost entirely of intact nitramine molecules, but decomposition before melting was directly detected in HMX. RDX was found to be a highly flexible molecule. In keeping with this flexibility, the

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crystal structure of the complex between RDX and sul*-lane revealed NNO_2 groups frozen in axial, equatorial, and planar positions within one molecule. The crystal structure of AZMTTC was determined and its thermal decomposition mechanism empirically reasoned. HNO_3, not previously recognized as a product, appears to trigger the decomposition of AZMTTC. Copious amounts of N_2O and CH_2O are then released due to depolymerization of the ring. The IR spectra of the gas and solid phases and the TGA all support this mechanism.

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I. Research Objectives

This research effort to discover the underlying chemical basis for the physical properties and chemical behavior of nitramines is multipronged in its thrust. Summarized below are the points of interest.

A. From the point of view of chemical mechanisms of the condensed phase behavior of nitramines the intention has been to investigate the molecular motion and phase transition characteristics of HMX. These studies involve approaches not previously used in this field such as ^{14}N nuclear quadrupole resonance, and rapid-scan Fourier transform infrared spectroscopy. Our objectives have now been essentially achieved in the case of HMX and RDX. The importance of intermolecular forces and the trapping of molecular fragments during the course of decomposition of HMX have been documented through this work. It was important to learn the extent to which these ideas also apply to other nitramines, such as RDX. To achieve this understanding, a ^{14}N NQR spectroscopy study of RDX was conducted. The molecular motion of RDX in the crystal lattice is greater than that in HMX suggesting that the intermolecular cohesive forces are overall smaller than those in HMX. This conclusion applies to the solid phase. A void exists in the description of RDX and HMX with respect to the nature of these compounds in the gas phase and the melt phase. Specifically, what is the chemical composition of RDX and HMX "melts"? What is the structure of RDX and HMX molecules in the "melt", solution, and gas phases? What is the structure of the β-RDX polymorph? These questions were addressed during the current grant year.

B. From the point of view of diagnostic molecular spectroscopy of a transient, reacting condensed phase material, we have expended considerable effort on developing techniques useful to problems that arise with energetic materials. Our intention has been to develop a technique that will provide a

large amount of data, is able to provide data in a relatively rapid time frame, and can be applied under high pressure and high heating rate conditions. Rapid-scan FT-IR spectroscopy has been our choice as this technique. Sample cells are being constructed that allow studies of rapid thermal decomposition processes. This work has broad chemical applications which has stimulated a great deal of interest outside the energetic materials community.

II. Progress Since Past Report

The bulk of the research during this past year has been described in detail in research publications and manuscripts forwarded to Dr. Len Caveny as they were finished. Only a highlighted summary with conclusions will be repeated here.

A. The molecular structure of the RDX molecule was ascertained by the use of FT-IR spectroscopy for the two solid phase polymorphs, α-RDX and β-RDX, in DMSO, CD_3CN, and acetone-d_6 solutions and in the vapor phase. These spectra are the first for vapor phase RDX and for the unstable β-RDX polymorph. The spectra reveal that RDX has essentially C_{3v} molecular symmetry in all of these environments except for the stable solid α-RDX polymorph where the symmetry is known from the neutron diffraction to be C_1. When given its freedom, the RDX molecule relaxes from the more strained C_1 symmetry to the C_{3v} symmetry in which all of the nitro groups become equivalent. The RDX molecule was also shown by variable temperature ^1H NMR and FT-IR spectroscopy to be extremely flexible when in the unconfined state. It is appropriate to think of RDX as able to distort readily when it is undergoing thermal decomposition.

B. The crystal structure of the 1:1 complex between RDX and sulfolane provides further evidence of the flexibility of RDX with respect to the

position of the NO_2 groups relative to the ring. All three NO_2 group positions (axial, planar and equatorial) are frozen in one molecule.

C. Great interest exists in knowing about the composition of RDX and HMX "melts." Virtually no experimental information is available on the real-time chemistry of this phase despite its importance to thermal decomposition and combustion of nitramine-containing propellants. By the use of rapid-scan FT-IR spectroscopy and a heating rate of $150°C$ sec^{-1}, the melt phase of both RDX and HMX were found to be largely composed of intact molecules. However, there is evidence of decomposition in the condensed phase of HMX before the melt layer forms. As the RDX and HMX melts age, hydroxymethyl formamide is the predominant liquid phase residue that remains. The structure of RDX and HMX molecules in the melt is similar to that found for these molecules in solution. HMX appears to adopt mostly a chair-chair ring conformation in the melt. RDX has essentially C_{3v} molecular symmetry in the melt. One might conclude from the fact that RDX shows little evidence of decomposition in the melt, that most of its decomposition takes place in the gas phase.

D. Examination of the gas-phase pyrolysis products of 1-methylazido-3,5,7-trinitraza-1,3,5,7-tetrazacyclooctane (AZMTTC) prepared by Frankel and Woolery of Rocketdyne was undertaken at various pressures from atmospheric to 500 psi using various heating rates from $5°C$ min^{-1} to $150°C$ sec^{-1}. Rapid-scan FT-IR spectroscopy of the gas phase revealed the important products of degradation and their change in concentration with temperature (time). Figure 1 shows the results. CH_2O and N_2O were previously reported to be the major products of pyrolysis of AZMTTC by mass spectrometry. They would normally arise if N-C ring bond cleavage were the major degradation pathway of AZMTTC. Early in the reaction we observe HN_3 in the gas phase at an amount which is competitive with the N_2O (Figure 1). The gas products of AZMTTC
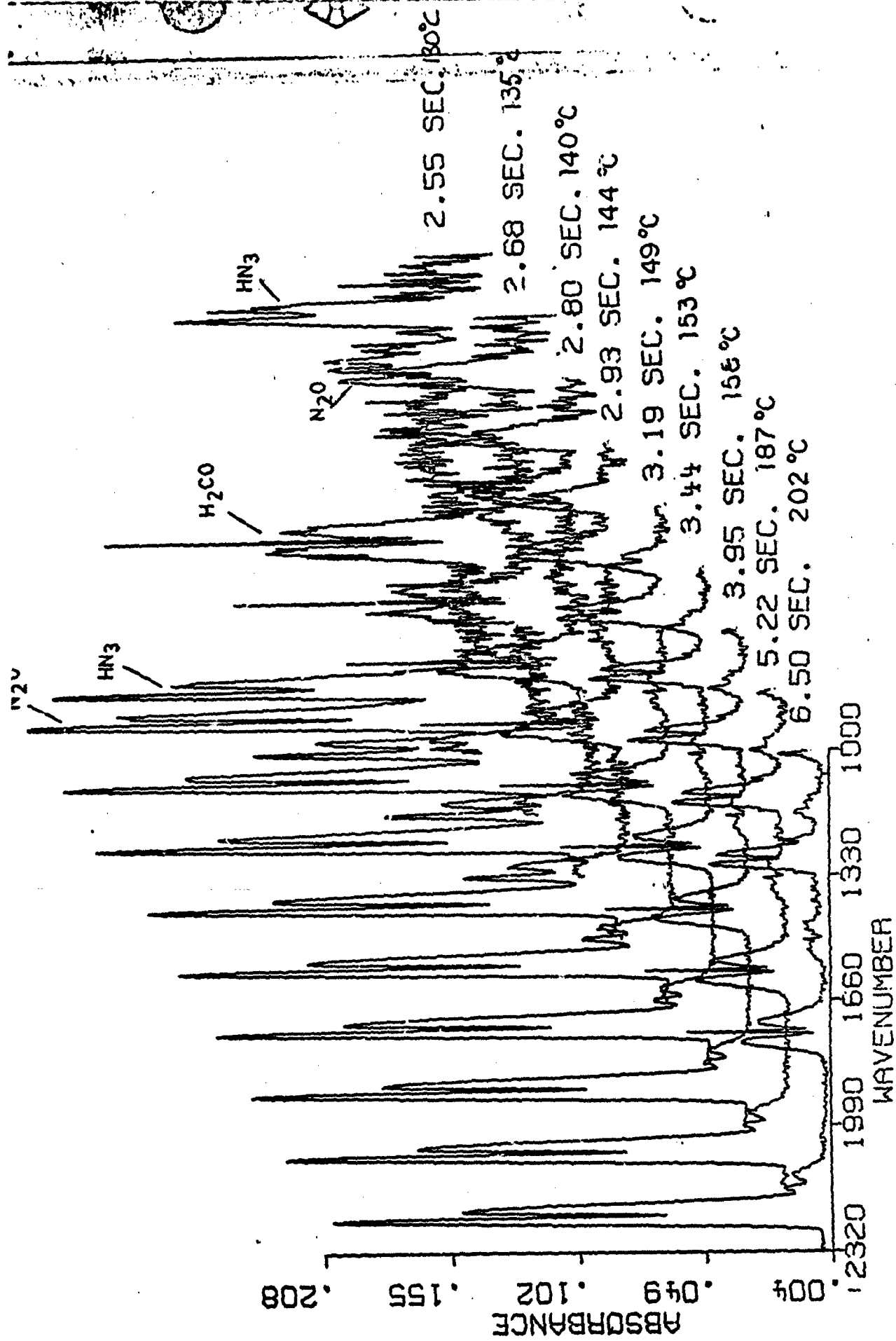
Figure 1.

decomposition are relatively independent of pressure which contrasts with RDX and HMX where the product distribution is quite pressure-dependent. HN_3 continues to be a product of pyrolysis throughout the degradation, but is less important relative to N_2O and CH_2O as the sample heats. The IR spectrum of the solid (Figure 2) during heating shows that the NO_2, CH_2 and ring modes of AZMTTC are rapidly lost which is consistent with the appearance of a large amount of N_2O and CH_2O in the gas phase. Although a certain amount of HN_3 is found in the gas phase, much of the azide is retained in the solid residue (perhaps as part of a polymer) as the CH_2O and N_2O are evolved. The TGA of AZMTTC supports these observations from the IR spectrum.

The crystal structure of AZMTTC reveals several features which help to explain the thermochemistry of the molecule. The relatively low decomposition temperature which is probably triggered by the evolution of some of the HN_3 is accentuated by the relatively few intermolecular cohesive interactions in the lattice compared to HMX. The azide group has no important intermolecular interactions which, when combined with an unusually long $C-N_3$ bond length, helps explain why HN_3 is so readily ejected from the AZMTTC molecule. The low temperature of decomposition results in the formation of CH_2O and N_2O as the other principal products, whereas in HMX, which decomposes about 150°C higher has much more oxidized fragments such as CO_2, CO, H_2O, NO, NO_2, etc., in addition to CH_2O and N_2O.

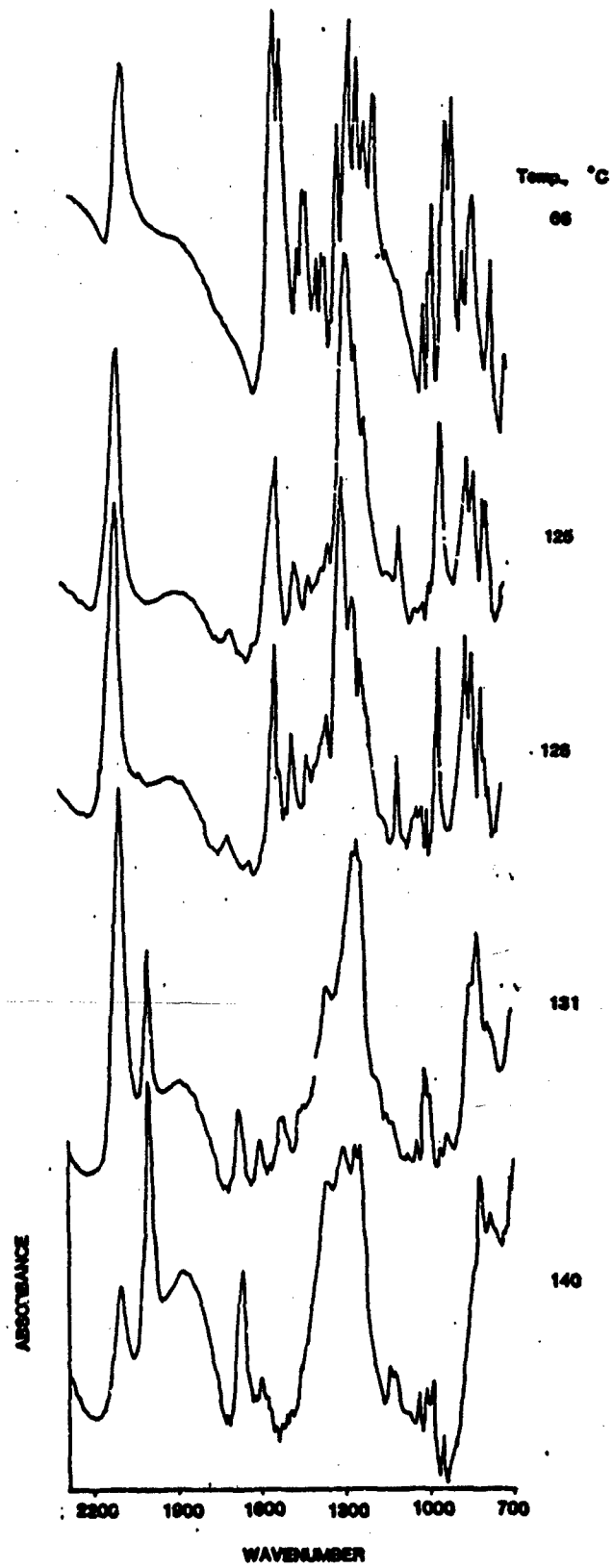Figure 2

III. Publications During Grant Year

A. Papers Appearing

1. R. J. Karpowicz, "Kinetic Data for Solid Phase Transitions by Fourier Transform Infrared Spectroscopy," Appl. Spec., 37, 79 (1983).

2. R. J. Karpowicz, L. S. Gelfand, T. B. Brill, "The Application of Solid Phase Transition Kinetics to Solid Propellants," AIAA J., 21, 310 (1983).

3. R. J. Karpowicz, T. B. Brill, "Librational Motion of Hexahydro-1,3,5-trinitro-s-triazine (RDX) Based on Temperature Dependence of the ^{14}N NQR Spectra: The Relationship to Condensed-Phase Decomposition," J. Phys. Chem., 87, 2109 (1983). (Selected for Flygare Memorial Issue).

4. R. J. Karpowicz, S. T. Sergio, T. B. Brill, "β-Polymorph of Hexahydro-1,3,5-trinitro-s-triazine. An FTIR Spectroscopy Study of an Energetic Material," Ind. Eng. Chem. Prod. R&D, 22, 363 (1983). (Invited by Editor).

B. Papers in Press

1. R. J. Karpowicz and T. B. Brill, "Comparison of the Molecular Structure of Hexahydro-1,3,5-trinitro-s-triazine (RDX) in the Vapor, Solution and Solid Phases," J. Phys. Chem.

2. T. M. Haller, A. L. Rheingold, and T. B. Brill, "The Structure of the Complex between Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and N,N-Dimethylformamide (DMF), $C_4H_8N_8O_8 \cdot C_3H_7NO$; A Second Polymorph," Acta Cryst.

3. T. M. Haller, A. L. Rheingold, and T. B. Brill, "Structure of the Complex Between Hexahydro-1,3,5-trinitro-s-triazine (RDX) and Tetrahydrothiophene-1,1-Dioxide (Sulfolane)," Acta Cryst.

IV. Personnel

1. Thomas B. Brill - Principal Investigator

2. Richard J. Karpowicz. Ph.D. Dissertation Defense held 11/14/83. Ph.D to be awarded in January 1984.

3. Yoshio Oyumi - 1st year Ph.D. candidate.

4. Thomas M. Haller. M.S. student.

V. Coupling Activities

Numerous conversations have been carried out over the telephone, at meetings and at workshops with people who are interested in our research. The meetings attended during the past year in which I discussed nitramine research were the AFOSR/AFRPL Contractor's Meeting (March), an ONR workshop on Polymers and Energy Release (July), and The Rocky Mountain Conference on Applied Spectroscopy (August).

I participated on a STAS review panel of the Army-BRL research program on liquid propellants in April and May along with five other academic chemists. I gave a special lecture on nitramines at Picatinny Arsenal in February.

We have been developing further contacts with NRL, NSWC, Rocketdyne and SRI concerning acquisition of new research nitramines.

I consult for Morton-Thiokol and receive IR&D research support from them for a promising research idea to incorporate metal complexes as homogeneous dopants in the HMX and RDX crystal lattices. Mr. Steve Palopoli is a graduate student in my group who is carrying out that research. The concept behind this research is an outgrowth of this AFOSR-sponsored research effort.

VI. New Discoveries

(1) The RDX molecule has the same structure in the vapor phase, in solution, in the melt phase and in the solid β-RDX polymorph. This is C_{3v} symmetry in which all of the NNO_2 groups are essentially equivalent. This structure differs from solid α-RDX in which C_s symmetry exists. As a result, when RDX decomposes the molecule is undergoing rapid intramolecular fluctuations which equilibrate all of the NNO_2 positions and all of the C-N bond positions.

(2) Spectroscopic research on the "melt" phase of RDX and HMX was conducted in a comprehensive manner for the first time ever this year. Fresh RDX and HMX "melts" are comprised of mostly intact RDX and HMX molecules.

However, more decomposition occurs in HMX than RDX before the melt forms. As the melt ages, hydroxymethyl formamide (HMFA) is the primary material that replaces the nitramine. However, HMFA is not a solvent for RDX when the melt initially forms. This discovery negates several of the conclusions of Batten and Cosgrove and Owen about the nature of RDX decomposition below and at the melting point. It may be proper to conclude that most of the decomposition of RDX actually takes place in the gas phase.

(3) An empirical mechanism for the thermal degradation of AZMTTC has been established. AZMTTC decomposition is triggered by the loss of HN_3. Following this step the nitramine portion of the molecule rapidly degrades yielding N_2O and CH_2O. The TGA, crystal structure and IR spectra of the solid and gas phase are all consistent with this mechanism.

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