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MOLECULAR DYNAMICS OF NITRAMINES AND HIGH ENERGY COMPOSITE MATE--ETC(U)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Determination of the pressure-temperature phase diagram of the beta-to-delta polymer conversion of HMX has been completed. Enthalpy, entropy values were determined as was the effect of particle size. Variations in the nature of decomposition were found to be the source of the observed slope breaks and the particle size effect. The mechanism of motion in beta-HMX up to the phase transition temperature was found to involve disruption of the pivoting motion about the most stabilizing intermolecular interaction in HMX. Studies on the

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I. Research Objectives

The research being conducted on this grant is a broad-based attack on understanding the kinetics and thermodynamics of solid-phase processes in nitramines, development of rational and systematic methods to control and alter the degradation of HMX, and development of diagnostic methods to study these phenomena. The specific objectives are detailed as follows:

AFOSR-80-0285

- The thermodynamics of the thermally interconvertible solid polymorphs of HMX is important in the mechanics, chemical decomposition and energy balance of rocket propellants. The thermodynamic parameters (ΔH, ΔS) of the $\beta \rightarrow \delta$ HMX transformation were determined up to a pressure of 100000 psi (620 MPa). The kinetic parameters of this transformation are being studied by Fourier transform infrared and Fourier transform nuclear quadrupole resonance spectroscopy. These techniques permit fast sampling of data from which the Arrhenius parameters of the $\beta \rightarrow \delta$-HMX conversion may be extracted. The Arrhenius data can be extrapolated to give rates at high temperature due to the fact that the $\beta \rightarrow \delta$ conversion is a tight-complex reaction. Knowledge of the energy and rate constant data will identify the conditions where it is necessary to include the $\beta \rightarrow \delta$-HMX conversion in performance and combustion modeling.

- Modification of the decomposition of HMX is vital to the future use of HMX. A great deal of time and expense has gone into attempts to modify HMX combustion by doping the crystal. Although the ionic crystal lattice of ammonium perchlorate can be readily doped in this way, HMX has not succumbed to the same approach. It is not surprising in retrospect that the approaches taken in this area have been unsuccessful. Very recently we have initiated a systematic study of the interactions in HMX which are responsible for the stability of the lattice.[1,2] This work has involved some computer graphics, mechanistic studies of motion in HMX, and now, with the acquisition of a single crystal X-ray diffractometer in the chemistry department, a crystallography study of HMX-solvates. The objective here is to identify the most susceptible sites in the HMX molecule for coordination by dopants. A dopant able to modify HMX combustion will be incorporated in the HMX lattice only if its size and coordination characteristics are compatible with the HMX molecule and crystal lattice. The lack of attention to this detail has resulted in slow progress in this area in the past. We are also looking at the nature of the HMX-TMETN two-phase system as a function of temperature using FT-IR. Because these two energetic materials are sometimes used together in propellants, the nature of the HMX polymorphs and the interactions between these two materials is of practical interest.

- Development of new methodology to examine the solid-phase events occurring in energetic materials is an important element in this research. It has been necessary to study decomposing solids under high pressure and high temperature and to develop methods that can provide detailed molecular information in a comparatively rapid time-frame. We are developing FT-nuclear quadrupole resonance as a technique for studying nitrogen-containing materials under high pressure and temperature.

II. Status of Research

A great deal of progress has been made in the area of thermodynamics of the β → δ-HMX conversion, and we consider that element now complete. Using Raman spectroscopy the β → δ transformation as a function of pressure and temperature was determined to the limit of 100000 psi (690 MPa) and 248°C. From the phase diagram, values of ΔH and ΔS were deduced. The effect of particle size (175 μm and 3 μm) of HMX in this transition was established.

Figure 1 summarizes the data obtained. The "dots" are 175 μm and the "squares" are 3 μm HMX. The β → δ phase transition is regular and normal below 30000 psi in 3 μm HMX, but then experiences an abrupt slope break. 175 μm HMX has the same appearance except that the break occurs at lower P and T. The origin of the slope break was shown (by Fourier transform-infrared and chemical ionization mass spectrometry) to result from the onset of decomposition in HMX. 175 μm HMX crystallites retain the decomposition products to a much greater degree than do the 3 μm crystallites. Hence 3 μm HMX gives a truer phase diagram below 30000 psi (207 MPa). However 3 μm HMX experiences extensive degradation above 240°C, and 30000 psi. This decomposition produces a severe disruption and expansion of the crystal lattice which allows the β → δ transition to occur very easily. Hence an abrupt slope-break is observed. ΔH calculated for 3 μm HMX above 245°C is about equal to the activation energy for the decomposition of HMX (250 KJ/mole). The β → δ-HMX transition and the decomposition of the molecule become thermally indistinguishable at this point. The specific conclusions reached are summarized in Part VI of this report.

Mechanistic studies of the molecular motion in β-HMX were computed up to a temperature of 156°C during the grant year. This research employed variable temperature ^{14}N nuclear quadrupole resonance spectroscopy. A spectrometer in the Physics Department at Hunter College of CUNY was used for this research. The experiment was significant to science because it was the first use of a recently discovered pulse technique known as SORC (strong off-resonance comb). The results showed the nature of molecular motion in β-HMX up to the β → δ transition temperature. The motion of the β-HMX molecule changes as temperature increases. All of the important motion involves a pivoting about the most important electrostatic interaction in HMX which is the interaction between the oxygen atoms of the axial NO_2 groups with the C-N-C ribbon of atoms on the axial region of neighboring molecules.[1] As the temperature approaches the β → δ transformation temperature, the HMX molecule experiences additional motion in a direction perpendicular to this interaction. As a result, the interaction is disrupted and the β-HMX lattice is destabilized with respect to conversion to the δ-HMX polymorph.

The rate data for the β → δ-HMX conversion have not been obtained as yet. Our FY-82 AFOSR support allows acquisition of the necessary equipment to conduct these studies. So far, a high-temperature cell has been constructed for the FT-IR spectrometer housed in the Department of Chemical Engineering. The first cell constructed was not able to withstand sustained heating using moderate N_2 gas flow. An improved cell is being constructed at this moment. We expect that in the next two months crude FT-IR data on the β → δ conversion rate will be available. In November 1981 we expect to have delivered the NQR spectrometer. It will be necessary to convert this instrument for Fourier transform studies, and to learn how to conduct solid-phase kinetic studies with it. However, with FT-NQR spectroscopy, spin-lattice relaxation times can be measured. From these accurate Arrhenius parameters can be calculated. The combination of FT-IR and FT-NQR should provide a kinetic and mechanistic basis for assessing the importance of the β → δ-HMX conversion in propulsion, deflagration and detonation conditions.

The research program on modifications of HMX is a new effort initiated in July, 1981. This research program is potentially one of the most important projects we can imagine in the area of HMX materials science. It could not develop in our research group without the background of molecular studies acquired with AFOSR support in recent years. We now see a way to systematically and rationally approach the problem of modifications to the HMX lattice. This research requires an accumulation of data on the electrostatic interactions that hold the crystal together. We have a smattering of the data already in the crystal structures of α, β and δ-HMX.[3-5] Much more data are needed. To this end, crystals of solvates of HMX involving N,N-dimethylacetamide, cyclopentanone, butanoic acid lactone, N-methyl-2-pyrrolidinone, and N,N-dimethylformamide[6] are being prepared. Single crystal X-ray crystallography of these solvates will further identify the electrostatically active sites on the HMX molecule that can be coordinated. Once this is done, we envision a synthesis program which is aimed at preparing transition metal coordination compounds that have size and electrostatics which are compatible with incorporation in the HMX lattice. This method will bring transition metal catalysts into the lattice and hopefully will permit alteration in the HMX degradation. Combustion studies on these doped materials can be conducted at Thiokol-Elkton. Because this project is just beginning, it is estimated that several years will be required to evaluate this new direction.

In connection with dopant studies, we have been investigating the HMX-TMETN system. β-HMX was found to dissolve in TMETN at elevated temperatures and to recrystallize upon cooling in polymorphs other than β-HMX. In this way we believe we have, for the first time, acquired crystals of -HMX. Little is known about this metastable polymorph because of the fact that its structure is unknown. If the crystals are good, we should be able to fill this void.

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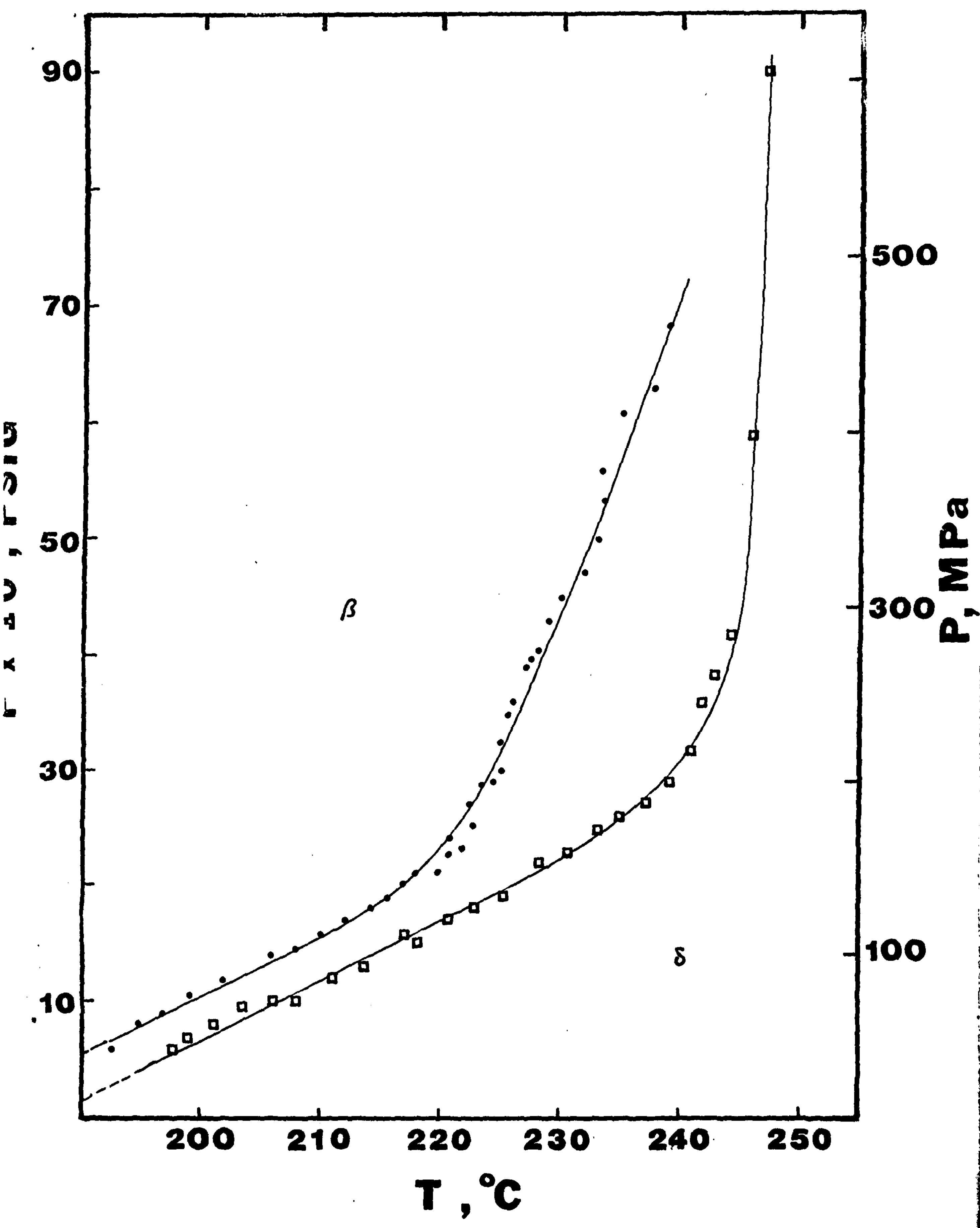
90
70
50
30
10
500
300
100
P, MPa
β
δ
200
210
220
230
240
250
T, °C

III. Publications

During the past year the following publications have been prepared.

A. G. Landers and T. B. Brill, "Pressure-Temperature Dependence of the β → δ Polymorph Interconversion in HMX," J. Phys. Chem., **84**, 3573 (1980).

A. G. Landers, T. B. Brill and R. A. Marino, "Electronic Effects and Molecular Motion in HMX Based on ^{14}N NQR Spectroscopy," J. Phys. Chem., **85**, 2618-2623 (1981).

R. J. Karpowicz and T. B. Brill, "The β → δ Transformation of HMX: Its Thermal Analysis and Relationship to Decomposition," AIAA Journal, submitted.

A. G. Landers, C. R. Dybowski and T. B. Brill, "Multiple-Pulse NMR Studies of α, β, γ, and δ-HMX Polymorphs: Interactions and Molecular Motions," in preparation.

R. J. Karpowicz and T. B. Brill, "The HMX-TMETN System: Phase Transitions of HMX in the Presence of Propellant Ingredients," in preparation.

IV. Personnel

A. Thomas B. Brill, Principal Investigator

B. Albert G. Landers, Graduate Research Assistant, Ph.D. in Chemistry awarded in August, 1981. Dissertation Title: "Thermochemical Studies of HMX."

C. Richard J. Karpowicz, Graduate Research Assistant; Ph.D. candidate in Chemistry now in his second year of graduate school.

D. Thomas J. Haller, Graduate Teaching Assistant and M.S. candidate in Chemistry now in his second year of graduate school.

V. Interactions

During the past year contacts have been maintained with AFRPL (Berge Goshgarian), NSWC (Wayne Elban, Explosion Physics Branch), Thiokol-Elkton (Winston Brundage and Frank Goetz) and The Thermophysical Laboratory at Purdue (Ray Taylor and Bob Shoemaker).

Research was presented at the "Workshop on Fundamental Research Direction for Decomposition of Energetic Materials" held in Berkeley, CA, in January 1981, and at the AFOSR-AFRPL contractors meeting held in Lancaster, CA, in March, 1981.

Research seminars on our HMX research were presented at SUNY-Plattsburgh in April, 1981, and the University of Richmond in September, 1981.

VI. The Most Important New Discoveries (Summary)

A. Thermochemical Studies at Elevated Pressure and Temperature

- δ-HMX was shown to be the stable polymorph of HMX above 248°C regardless of the pressure on the system.
- Enthalpy and entropy values for the β → δ HMX transformation have now been established up to 100000 psi (690 MPa).
- 3 μm HMX is found not to retain decomposition products nearly to the extent that larger particle sizes can. Hence, the decomposition of 3 μm HMX is not complicated by secondary decomposition reactions to the extent that larger particles are. 3 μm HMX should be the particle size of choice in all decomposition studies.

B. Mechanisms and Kinetics Studies of the β → δ Conversion

- The fundamental motion of interest when the β → δ transition occurs involves disruption of an oxygen to C-N-C intermolecular interaction. This interaction is the key to the stability of the β-HMX lattice.

C. Ingredient Studies

- HMX undergoes a recrystallization process to new polymorphs in the presence of the energetic plasticizer, TMETN. This phenomenon may be important in both the manufacture and the combustion modeling of HMX-TMETN based propellants.