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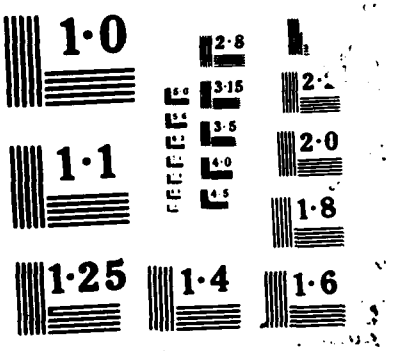
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KINETIC MEASUREMENTS OF THERMAL DECOMPOSITION OF ENERGETIC MATERIALS AT HIGH PRESSURES

FINAL REPORT

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)
A new spectroscopic method was developed which permits kinetic measurements of reactions in energetic materials at high pressures. The method utilizes FTIR in conjunction with a diamond anvil high pressure cell. Measurements were made on HMX and nitromethane. The rate of thermal decomposition for HMX was found to have a negative pressure dependence, which, when coupled with the observed thermodynamic activation quantities, led to a unimolecular decomposition mechanism - ring expansion prior to bond scission. Contrary to the HMX case, the decomposition rate for nitromethane was observed to have a positive pressure dependence leading to a bimolecular reaction mechanism which is the result of increased intermolecular interactions. A dynamic stress-induced catastrophic reaction was observed in protonated nitromethane at room temperature, but not in the deuterated from.

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FINAL REPORT

During this 3 year program, October 17, 1984 to October 16, 1987, the following was accomplished:

(1) A new spectroscopic method was developed for measuring the kinetics of thermal decomposition of energetic materials as a function of pressure and temperature. A Fourier transform infrared absorption measurement technique is used in conjunction with a diamond anvil high pressure cell modified for temperature capability. The method has wide applicability and can be used to study the effects of pressure and temperature not only on thermal decomposition reactions of energetic materials, but also on chemical reactions in general.

(2) The above method was used successfully to study the thermal decomposition kinetics of HMX and nitromethane at high pressures and provided data on these materials which never had been obtained before. For example, information such as reaction rates, activation energies, volumes, entropies and free energies provided the basis for proposing molecularity and reaction mechanisms at pressures in the range of those existing for detonation conditions.

(3) For HMX, pressure was found to decrease the rate of thermal decomposition, while temperature increases the rate in typical Arrhenius behavior. The volume of activation was found to be positive (3%), indicating that the reaction mechanism is unimolecular and probably involves a ring expansion prior to bond scission. The observed combined pressure dependencies appear to explain why β HMX can detonate at high pressures.

(4) In contrast, for nitromethane both temperature and pressure were found to increase the rate of thermal decomposition indicating an overall bimolecular reaction mechanism. However, the mechanism, unlike β HMX, is complex and appears to vary over large changes in pressure. A chemical mechanism is proposed which explains the bimolecularity and also accounts for the observed decomposition products, ammonium formate and water.

(5) In collaboration with P. J. Miller (NSWC), the effect of pressure on the vibrational spectra of these materials was also measured. From such data a complete normal coordinate calculation for nitromethane was performed. A softening of the frequency of the asymmetric stretching mode of NO_2 with increasing pressure indicated a strong intermolecular interaction. The shifts of the normal modes of the NO_2 stretching vibrations were calculated as a function of density and pressure using a minimum energy pair configuration and applying 2-site exiton theory. The results support the bimolecular nature of the thermal decomposition mechanism of nitromethane under high pressure.

(6) The pressure-temperature phase diagrams including melting point and chemical reactivity of these materials has been determined. The equation describing the pressure dependence of the melting point of nitromethane is $T=100\ \ln(P)+389.2$,
where T is in degrees Kelvin and P is in GPa. The curve could only be determined to 1.54 GPa and 433K because nitromethane rapidly decomposes above these conditions.

(7) A dynamic stress-induced catastrophic reaction was observed at room temperature in protonated nitromethane which appears to be crystal orientation dependent with respect to the applied axial load. Single crystals grown from the liquid with the 111 and either the 001 or the 100 crystal faces perpendicular to the applied load direction in the pressure cell, when pressed rapidly to over 3 GPa, exploded instantaneously accompanied by an audible snapping sound. The normally transparent sample becomes opaque. The retrieved solid residue appears to be amorphous and stable when heated to temperatures $>300^{\circ}C$. The same phenomenon was not observed in deuterated nitromethane.

(8) Three papers listed below were prepared for publication as a result of this work.

(a) **"Effects of Pressure and Temperature on the Thermal Decomposition Rate and Reaction Mechanism of β-Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine"**, by G. J. Piermarini, S. Block and P. J. Miller, J. Phys. Chem., 3872 (1987).

(b) **"Effects of Pressure on the Thermal Decomposition Kinetics and Chemical Reactivity of Nitromethane"**, by G. J. Piermarini, S. Block and P. J. Miller, submitted to Journal of Physical Chemistry, January 12, 1988.

(c) **"Effects of Pressure on the Vibrational Spectra of Liquid Nitromethane"**, by P. J. Miller, S. Block and G. J. Piermarini, submitted to Journal of Physical Chemistry, January 12, 1988.

(9) In March 1987, an invited talk entitled " The Effects of Pressure and Temperature on the thermal Decomposition Reaction of HMX" was given at the Working Group Meeting on Sensitivity of Explosives (ARO),-CETR, New Mexico Tech, Soccorro, NM. Another invited talk entitled " The Effects of P and T on the Thermal Decomposition of Energetic Materials" will be given in June 1988 at the Gordon Conference on Chemistry of Energetic Materials, New Hampton School, New Hampshire. Another talk entitled "Pressure Effects on Nitromethane: Reactivity, Compressibility and Vibrational Spectroscopy", will be presented at the March 1988 American Physical Society Meeting in New Orleans.

As the three year funding period has expired, no further work under the present program is possible. However, because of the great potential the method has for furthering our understanding of the science behind detonation processes of energetic materials, a proposal to continue this work for another three year period has been submitted to ARO.

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