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The $\beta \rightarrow \delta$ Transformation of HMX: Its Thermal Analysis and Relationship to Propellants

Richard J. Karpowicz* and Thomas B. Brill†
University of Delaware, Newark, Delaware

The pressure and temperature sensitivity of the $\beta \rightleftharpoons \delta$ polymorph conversion of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) has been studied by Raman spectroscopy up to 620 MPa (90,000 psig) and 248°C. The particle size dependence and slope breaks previously discovered in the pressure range up to 138 MPa (20,000 psig) are more pronounced at higher pressure and temperature. The dependence on particle size and the slope breaks are shown to be associated with decomposition products trapped in the crystal lattice. Trapped decomposition products destabilize β-HMX with respect to conversion to δ-HMX. Because 3-μm HMX does not retain the decomposition products, it yields a true $\beta \rightarrow \delta$ conversion line. $\Delta H = 13$ kJ/mole is found for the transition in 3-μm HMX. At about 240°C and 207 MPa (30,000 psi) 3-μm HMX decomposes and ΔH rises rapidly to a limit of 232 kJ/mole which is similar to E_a for the decomposition of HMX. The $\beta \rightarrow \delta$ transition and decomposition occur simultaneously in this region. Above 248°C β-HMX converts to δ-HMX regardless of the pressure.

Introduction

THE compound octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is an important nitramine solid rocket propellant. It exists in four solid phase polymorphs, labeled α, β, γ, and δ-HMX (Refs. 1-3). β-HMX is the room temperature stable form which is used in propellant manufacture. Solid β-HMX converts to the high temperature stable form, δ-HMX, at 163°C.[1-3] Figure 1 shows the ring conformation change that accompanies the $\beta \rightarrow \delta$-HMX transformation.[4] Pressure also induces conversions between HMX polymorphs.[5] Of notable importance is the observation that increasing pressure will convert the less dense polymorph, δ-HMX, to a more dense form, β-HMX. Thus, pressure and temperature are opposed forces in the $\beta \rightleftharpoons \delta$ conversion.

A change in volume and enthalpy as well as microfracturing accompanies the polymorph interconversion. These effects may produce profound perturbations to the mechanical and combustion characteristics of HMX.

First, fracturing beneath the surface of burning HMX crystals has been observed[6-8] and, in part, may be due to the stress of the $\beta \rightarrow \delta$ solid phase transition. Second, a serious concern in the rocket propulsion field is uncontrolled reactions that result from high-pressure transient phenomena. Pressure and temperature-induced solid phase changes leading to enthalpy changes and stress fracturing below the burning surface are important to deflagration-to-detonation (DDT) phenomena and hazards technology.[9] DDT processes can be initiated at 345 MPa (50,000 psi) or less.[10] Third, solid phase transitions might play a role in the change in the pressure exponent observed in HMX monopropellants over the range of 6.9-345 MPa (1,000-50,000 psi).[11] Fourth, if the size of the HMX particles is large compared to the thermal wave thickness of the burning surface, then complicated pressure-temperature gradients in the crystal could contribute to differences in stability and burn rate which depend on the HMX particle size.

We have recently characterized the $\beta \rightleftharpoons \delta$-HMX transformation in the pressure range of 0.1-138 MPa (0-20,000 psig) and the corresponding temperature range of 165-210°C.[3] This pressure encompasses that present during propellant combustion. The phase transition was found to depend on the particle size of HMX with β-HMX being somewhat more stable as the particle size diminishes. In addition, a slope break in the $\beta \rightarrow \delta$ conversion line was observed at 69 MPa (10,000 psig) and 200°C for mean particle sizes >50 μm, but no slope break occurred with 3-μm HMX. A particle size dependence and the presence of slope breaks in the phase transitions preclude extrapolation of the transition line into the pressure range of deflagration and armament applications. Based on this lower pressure range, we were not able to specify the source of the slope breaks or the particle size effects.

The present project was initiated after the addition of a second stage to the pressure intensifier system. This improvement extended the pressure range to 690 MPa (100,000 psig). The effect of pressure and temperature on the $\beta \rightarrow \delta$-HMX conversion in 175-μm and 3-μm HMX at higher pressure is much more dramatic than in the lower pressure range. Clear particle size effects are witnessed. In order to characterize the chemical changes that occur when HMX has been subjected to this thermal and pressure stress, mass spectral, and thermogravimetric analyses were made. The results cast light on the role of the decomposition in the $\beta \rightarrow \delta$ conversion of HMX. The probable source of the differences in the stability of HMX as a function of the particle size has been identified. Enthalpy values are reported for the $\beta \rightarrow \delta$ transition through its entire pressure-temperature range.

Experimental

Samples of β-HMX with a mean particle size of 175 μm and 3 μm were used without further treatment. However, to determine if residual impurities, such as RDX (hexahydro-1,3,5-trinitro-*s*-triazine), affected the $\beta \rightleftharpoons \delta$ phase transition, a sample of 175-μm HMX was extracted with 1,2-dichloroethane for 48 h. The residual HMX was washed with acetone and dried in a vacuum oven. HMX purified in this way produced the same results as the unpurified material.

Instrumentation

Raman spectra used to diagnose the phase transition were recorded on a Spex 1401 double monochromator spectrometer interfaced to a Nicolet 1180 data acquisition system. A Spectra Physics 4 W Ar$^+$ laser tuned to 488.0 nm and a power output of 0.3 W was used for excitation. The monochromator slits were set at 150 μm. Usually three scans were averaged to improve signal quality.

The methane chemical ionization (CI) mass spectrometry was carried out on a DuPont 21-492B double focusing mass spectrometer. The source and pumping system had been

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*Graduate Research Assistant, Department of Chemistry.

†Professor of Chemistry, Department of Chemistry.

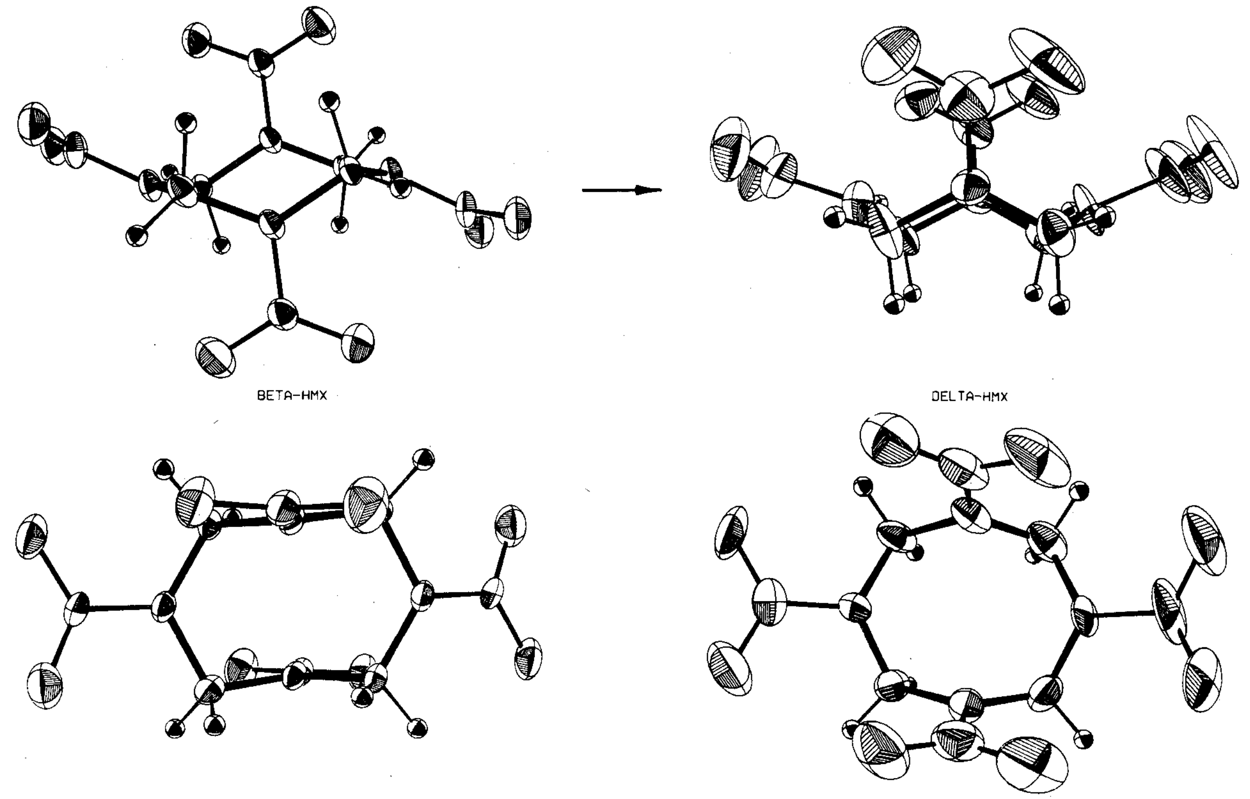

Fig. 1 Equivalent projections of β and δ-HMX molecules showing the atom position changes that occur in a β to δ transition. Both a side and top view of the molecules are shown.

modified for the CI mode. The source pressure was 67 Pa (0.5 Torr) and the source temperature was 220°C. A homebuilt pyrolysis probe was controlled by a Teco temperature programmer and temperature indicator. Data acquisition was accomplished with a Hewlett-Packard 21MX computer. The scan rate was 2 s/decade and the probe heating rates were either 2.5°C/min or 5°C/min. A mass region from 41 to 517 was scanned.

Pressure-Temperature Experiment

The pressure-temperature characteristics of the $\beta \rightleftharpoons \delta$ transformation in HMX require consideration of sample history, heating rates, and heating times. These nuances were parameterized in our prior study of the lower pressure and temperature side of the transformation.[3] The details of the present experiment are described here with this background.

In order to obtain the pressures up to 690 MPa (100,000 psig) an N_2 gas inlet pressure of 14 MPa (2000 psig) was boosted to 138 MPa (20,000 psig) with a Haskel Engineering AG-152G single-acting single-stage air driven intensifier. This 20,000 psig gas was then used to drive a Harwood Engineering A255 single-acting oil driven intensifier to a maximum pressure of 690 MPa (100,000 psig). The pressure was monitored with a calibrated manganin cell.

The sample holder was a 316 stainless-steel (SS) tube 10.0 cm in length and having a wall thickness of 0.46 cm. The tube was sealed at one end with a set screw possessing a specially ground concave end to reduce the pressure strain. The tube end was then heli-arc welded. A 1.4 × 100 mm glass capillary containing the HMX sample fit snugly inside the steel tube and experienced efficient and reproducible heat transfer according to thermocouple measurements.

For heat the SS tube was tightly fitted into an Al block containing four 200 W cartridge heaters. The temperature was regulated by an Omega 8000 m time proportioning controller and monitored with a Fluke 2100A digital thermometer. The temperature readings were accurate to within ±0.2°C. The temperature inside the glass capillary tube was determined by placing a thermocouple in the capillary and inserting it into the cell. When the cold SS tube was placed in the heating block, the temperature in the capillary reached the block temperature at 220°C within 90 s.

The pressure-temperature dependence of the polymorph interconversion was determined on 10 mg samples of HMX by pressurizing to the desired pressure and placing the cell in the heating block pre-set to the desired temperature. After 4 min the heating block was quickly removed and the sample depressurized. Because hysteresis exists in the polymorph transformations of HMX, the polymorph present under the elevated pressure and temperature conditions remains for at least 12 h.[3]

The Raman spectra in the ring torsion region (300-500 cm^{-1}) was used to distinguish the polymorphs of HMX.[12] By repeating the procedure on fresh samples of HMX and increasing the pressure each time in 6.75-MPa (1000-psig) increments, the conditions where the δ polymorph was no longer present could be determined. Figure 2 shows the Raman spectra typically obtained. The Raman spectrum at 25°C and atmospheric pressure shows bands due to pure β-HMX.[12] At 187°C and atmospheric pressure, β-HMX completely converts to δ-HMX. As the pressure on the sample is increased, the δ-polymorph gradually converts to the β-polymorph. The conversion to β-HMX is complete at a pressure of 37.1 MPa (5500 psig). At least three Raman scans were averaged because sample deterioration reduced the quality of the spectra. However, it was found that agitation of the 175-μm samples prior to recording the Raman spectrum improved the spectral quality. Agitation appears to increase the homogeneity of the sample and thereby better reveals the extent of the $\beta \rightleftharpoons \delta$ transformation. Agitation was not necessary for 3-μm HMX.

Results

Our previous study on the $\beta \rightleftharpoons \delta$ transition of HMX covered the pressure range of 0-138 MPa (0-20,000 psig) with an accuracy of ±1.4 MPa (±200 psi).[3] It revealed two important features: β-HMX becomes more stable with respect to

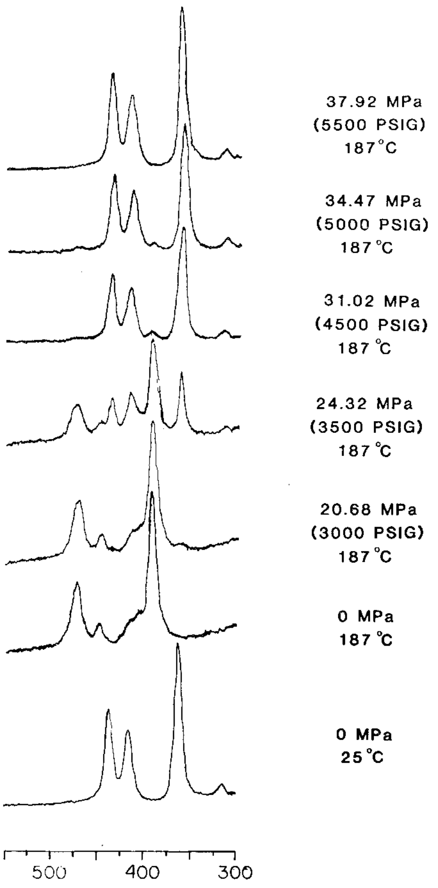

Fig. 2 Raman spectra of the ring torsion region of HMX as a function of pressure along the 187°C isotherm. A 5-min heating time was employed for each spectral scan. A δ→β-HMX phase transition occurs as the pressure is increased.

transformation to δ-HMX as the particle size diminishes, and a slope break occurs at 69 MPa (10,000 psig) for mean particle sizes >50 μm. No slope break was detected with 3-μm HMX.

The dependence of the β⇌δ-HMX interconversion on pressure up to 620 MPa (90,000 psig) and temperature up to 248°C was determined in this work and is shown in Fig. 3. The two-stage gas booster used in gathering these data is somewhat less accurate ±6.9 vs ±1.4 MPa (±1000 vs ±200 psi) than the single stage system and, therefore, some of the finer details known to exist in the 0-138 MPa (0-20,000 psig) region are obscured. However, the particle size dependence is still readily apparent. The β→δ transformation takes place at a higher temperature for a given pressure in 3-μm HMX than it does in 175-μm HMX. This means that β-HMX is more stable toward transformation in the smaller particle sizes than it is in the larger sizes. The effect becomes much more pronounced above the 138 MPa (20,000 psig) and 220°C.

A second striking feature in Fig. 3 is the slope break observed at 138 MPa (20,000 psig) and 220°C in 175-μm HMX and at 207 MPa (30,000 psig) and 242°C in 3-μm HMX. A critical temperature (248°C) is reached in 3-μm HMX above which, regardless of the pressure, the δ-polymorph is the stable form. Because no other polymorphs were detected, the presence of slope breaks in the transition line suggests that other chemical or mechanical events take place with these conditions of pressure and temperature.

Discussion

The Role of Decomposition

The remarkable slope breaks in the β→δ-HMX conversion as well as the particle size effects seen in Fig. 3 are intimately related to the solid phase decomposition of the HMX. The

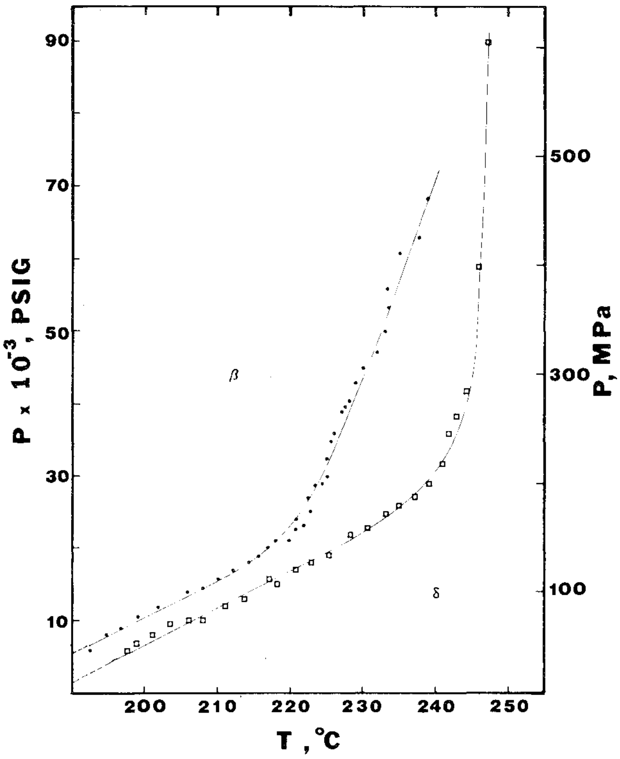

Fig. 3 The transition line of β⇌δ-HMX chosen at the conditions where δ-HMX can no longer be detected. (●) 175-μm HMX; (□) 3-μm HMX.

first clue to this fact is the color of 175-μm HMX compared to that of 3 μm after heating in the 220-240°C region and pressurizing in the 138-483 MPa (20,000-70,000 psig) region. Definite discoloration occurs in the 175-μm samples while 3-μm HMX remains essentially colorless. Of course, this visual observation is hazardous because the reflection of visible light from 3-μm HMX is expected to be much greater than that from 175-μm HMX. Hence, less of the incident light is available for absorption by chromophores in the 3-μm particles. They could appear to the eye to have undergone less decomposition. Primary and secondary decomposition products, such as NO_2, CH_2NNO_2, CH_2O, N_2O, amides and depolymerization fragments, have been identified in the solid and liquid phase degradation of HMX.[13-20]

If the extent of decomposition is different between the two particle sizes, it should be analytically detectable. A chemical ionization (CI) mass spectral analysis was made of 5-μg quantities of untreated 175-μm and 3-μm HMX. Very carefully defined parameters are needed to obtain reproducible and comparable mass spectra on HMX and these requirements will be published elsewhere.[21] A sample of 175-μm HMX was pressurized to 407 MPa (59,000 psig) and heated to 234°C for 4 min. This pressure-temperature combination produces conditions along the β→δ transition line for 175-μm HMX. The Raman spectrum was recorded to verify that the sample was β-HMX. A similar pressure-temperature experiment was conducted on 3-μm HMX at 234°C except that the pressure was held along the phase transition line at 193 MPa (28,000 psig). A profile of the total ion current (mass 41 and higher) as a function of temperature (time) was obtained on these pressure-temperature treated samples. The mass spectral conditions were the same in all cases. Figure 4 shows the results. The mass spectrum of untreated β-HMX and the 3-μm HMX subjected to pressure and temperature have essentially equivalent profiles. For these two samples the ion current is produced mostly by vaporization of the HMX molecules and rises until the sample is nearly expended. On the other hand, 175 μm exhibits a substantial ion current at 164°C before the vaporization of the HMX molecules begins. We attribute this low temperature maximum in the ion current to volatilization of trapped decomposition products. A close examination of the ion current for the treated 3-μm HMX shows a small low temperature maximum from trapped decomposition products, but considerably more trapped material is present in the 175-μm crystals. The volatile products are released when the 175-μm crystals, which have been strained by the pressure-temperature cycling through the $\beta \rightarrow \delta \rightarrow \beta$ polymorph transitions, fracture on heating in the mass spectrometer.

Thermogravimetric analysis (TGA) was conducted under vacuum on the HMX samples to support the mass spectral evidence of trapped material. It was found that a substantial fraction of the pressure-temperature conditioned 175-μm HMX samples is lost at the temperature at which the initial peaks in the ion current profile appear (160±5°C). Untreated HMX and pressure-temperature treated 3-μm HMX show no weight loss until the HMX begins to vaporize. These observations concur with the mass spectral data and imply that 175-μm HMX contains a considerable amount of trapped volatile decomposition products.

Mass spectra obtained at 164 and 200°C during the experiments of Fig. 4 exhibit similar fragments, indicating that the decomposition products released at 164°C do not markedly differ from HMX itself at 200°C. In 175-μm HMX it is important to stress that these trapped neutral decomposition products, whatever their nature, are probably a result of multiple reactions. It is known that primary decomposition products react with the parent molecules.[16] On the other hand, the surface-to-volume ratio of 3-μm HMX particle size is sufficiently large that volatile decomposition products are not retained in the crystals. Thus the color, the mass spectra, and the TGA results show little evidence of decomposition for the 3-μm particle size.

The Origin of Slope Breaks

One of the most notable features seen in Fig. 3 is the slope breaks in the phase transition lines. Slope breaks are often attributable to new polymorphs, but none occur in this system. Rather it is the decomposition process that creates the slope breaks. In 175-μm HMX only a small amount of decomposition takes place up to about 215°C and 138 MPa (20,000 psig). In the neighborhood of 220°C decomposition becomes sufficiently pronounced to cause a decisive slope break. The enthalpy change, ΔH, for the $\beta \rightarrow \delta$ transition in this particle size can be computed from the Clausius-Clapyron equation [Eq. (1)]. This equation was parameterized as described previously.[3]

$$dP/dT = \Delta H/(T\Delta V) \tag{1}$$

Table 1 summarizes the values of ΔH and ΔS computed for the 190-220°C range. The 175-μm ΔH value of 14 kJ/mole endothermic is approximately the average of the two ΔH values calculated from our earlier more accurate data, which show a small slope break at 200°C.[3] Above the slope break found in the 225-240°C region of 175-μm HMX, the $\beta \rightarrow \delta$ transition is not a "phase diagram" because the crystal lattice, and hence the phase transition, is altered by decomposition. In the previous study covering the lower temperature region, a small but reproducible slope break was observed at 210°C.[3] This break was not attributed to decomposition because none was detected in the mass spectrum. We now believe that 175-μm HMX experiences enough decomposition at or above 200°C to be detected in the form of phase diagram slope breaks, but that the decomposition fragments in the mass spectrum are virtually indistinguishable from the HMX fragments.

The possibility that pressure and/or temperature dependence of ΔH contributes to the slope changes was also considered, although the abruptness of the breaks casts doubt on this as an important factor. It is unlikely that temperature has a significant effect on ΔH in the 55°C range over which these data were taken. Pressure might be important. The influence of pressure on enthalpy is given in Eq. (2).

Table 1 Enthalpy and entropy changes calculated for the $\beta \rightarrow \delta$-HMX transition shown in Fig. 3

Particle size	Temperature, °C	ΔH,[a] kJ/mole	ΔS,[b] J/(K mole)
175 μm	190-220	14	33
	225-240	64	149
3 μm	196-235	13	31
	237-247	232	539

[a] Calculated with the equilibrium transition temperature of 431 K. [b] Calculated assuming equilibrium conditions. A decimal error in Ref. 3 has been corrected in these values.

$$\left(\frac{\partial H}{\partial P}\right)_T = V_0(1-\beta P)(1-\alpha T) \tag{2}$$

α is the thermal expansivity and β the isothermal compressibility. We are unaware of values of α and β for HMX. α should be essentially the same for the two phases of HMX and, thus, is an insignificant factor. Typical values of β are about $10^{-5}/\text{cm}^3$ for organics[22] and so βP might become significant at high pressure. However, the appearance of abrupt slope breaks rather than gradual curvature of the phase transition lines in Fig. 3 suggests that this is not the main factor in the phase transition behavior.

The phase transition of 3-μm HMX is probably closest to the true $\beta \rightarrow \delta$ transformation. The evidence gathered in this work indicates that at least below 235°C, the transition is unencumbered by decomposition considerations. The enthalpy change below 235°C is given in Table 1. Above 235°C a dramatic slope break is observed because additional events occur. The transition becomes highly insensitive to temperature. In fact, *above a critical temperature of about 248°C, δ-HMX appears to be the stable polymorph regardless of the applied pressure.* An enthalpy change can be calculated in the 245-248°C range. The resulting value of 232 kJ/mole is comparable to several of the covalent bond energies in the HMX molecule (e.g., N−N=200 kJ/mole, C−N=252 kJ/mole)[19] and to the activation energy for the thermal decomposition of HMX (about 210 kJ/mole).[20] We conclude that *the β→δ-HMX phase transition above 240°C and 207 MPa (30,000 psig) is necessarily accompanied by significant chemical decomposition, and that the two processes become thermally indistinguishable.*

It is interesting to note that the critical temperature of 248°C is approximately equal to the melting point of β-HMX which was obtained on superheated β-HMX crystals.[1] The similarity in temperature is regarded as fortuitous and not significant. The enthalpy of fusion of HMX is approximately 40 kJ/mole[23] which implies that the melting point will increase substantially with the application of pressure. The melting point of RDX, for example, increases markedly with increasing pressure.[24] There is no evidence of melting in the HMX samples.

Effects of Particle Size

A second important result shown in Fig. 3 is the appearance of a particle size effect. This was noted in our previous study[3] but is much more dramatic in the present one. It can be concluded that β-HMX is more stable with respect to transformation to δ-HMX in the 3-μm particle size than in the 175-μm size. This circumstance can now be attributed to the effects of decomposition. The existence of trapped decomposition products in the 175-μm HMX crystal lattice destabilize the lattice by disrupting the electrostatics. In effect the density will decrease slightly. If the lattice becomes less dense and the cohesive forces are disrupted, HMX will favor conversion to a less dense polymorph. It is believed that this is

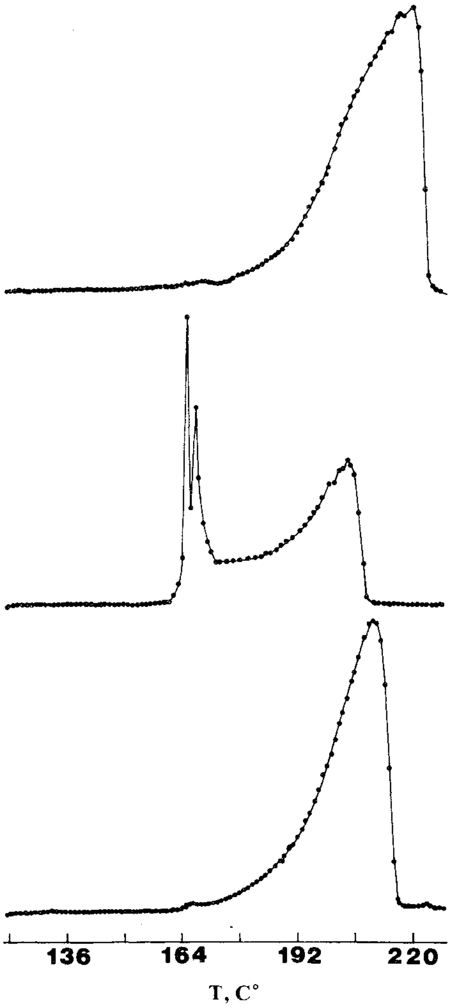

Fig. 4 The total ion current profile mass 41 and above of HMX samples as a function of temperature and taken under CH_4-CI conditions. Untreated HMX (top); 175-μm HMX which had been heated to 234°C and pressurized to 59,000 psi (middle); 3-μm HMX which had been heated to 234°C and pressurized to 28,000 psi (bottom). The apparent structure at 164°C in the 175-μm sample may or may not be real.

the reason why β-HMX (the more dense form) converts more readily to δ-HMX (the less dense form) as the particle size is increased. A "left-shifting" of the phase transition line will occur in Fig. 3 with an increase in the particle size.

A paradox might appear to exist in relationship between polymorph stability and particle size. If β-HMX becomes more stable as the particle size diminishes, would it be extraordinarily stable if the particle became extraordinarily small? From the point of view of small particles, β-HMX is indeed more stable with respect to conversion to δ-HMX. Of course, as the particle size diminishes to the extreme limit of isolated molecules, there is no lattice to speak of. The distinction between β and δ-HMX has chemical significance only when enough molecules aggregate to form a true crystal lattice. A model of the isolated HMX molecule reveals that the two ring conformations represented by β-HMX (chair) and δ-HMX (chair-chair) are interconvertible by a very low energy pseudorotation of the ring. Thus, no paradox exists.

Conclusions

There is an indication from the results here that slow decomposition of HMX is particle size dependent. With large particle sizes the degradation products in the interior of the grain are not released from the particle. They remain trapped where they can catalyze further decomposition. Hence, the products eventually observed are not likely to arise solely from the primary decomposition process. If mechanistic detail is sought, decomposition studies should be conducted on the smallest particle sizes possible. By the same token, the retention of decomposition products within larger HMX particles should cause them to decompose more rapidly and be less stable overall than small particles of HMX under the same conditions of pressure and temperature.

A critical temperature, about 248°C, is reached in the $\beta \rightleftharpoons \delta$ transformation above which, regardless of the pressure, β-HMX is unstable with respect to conversion to δ-HMX. δ-HMX appears to be the polymorph of thermodynamic interest in all applications above this temperature regardless of the pressure. The polymorph conversion and thermal decomposition occur simultaneously. The pressures exceed those present in propellant combustion and are in the range of deflagration and DDT conditions and armament applications, but the temperatures are considerably below the combustion range. Therefore, the question remains as to whether the $\beta \rightarrow \delta$-HMX transformation is fast enough to occur in practical situations. Some mechanistic details have already been presented,[25] and a study of the kinetics of these solid phase reactions is now complete. The results indicate that the transition is extremely fast at temperatures of burning HMX.[26]

Acknowledgments

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