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Coefficient of Thermal Expansion of the Beta and Delta Polymorphs of HMX

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Coefficient of Thermal Expansion of the Beta and Delta Polymorphs of HMX

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Abstract

Dimensional changes related to temperature cycling of the β and δ polymorphs of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) are important for a variety of applications. The coefficient of thermal expansion (CTE) of the β and δ phases are measured over a temperature range of –20˚C to 215˚C by thermo-mechanical analysis (TMA). Dimensional changes associated with the phase transition were also measured, and the time-temperature dependence of the dimensional change is consistent with phase transition kinetics measured earlier by differential scanning calorimetry (DSC). One HMX sample measured by TMA during its initial heating and again three days later during a second heating showed the β-to-δ phase transition a second time, thereby indicating back conversion from δ-to-β phase HMX during those three days. DSC was used to measure kinetics of the δ-to-β back conversion. The most successful approach was to first heat the material to create the δ phase, then after a given period at room temperature, measure the heat absorbed during a second pass through the β-to-δ phase transition. Back conversion at room temperature follows nucleation-growth kinetics.

Keywords: HMX, solid-solid phase transition, kinetics, thermal expansion, DSC, TMA

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1. Introduction

The chemical compound HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is an important nitramine monopropellant [1]. Initially HMX was discovered as a by-product from the synthesis of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) by the Bauchmann process [2]. Bauchmann [3-5] and co-workers showed that the nitrolysis of hexamine with ammonium nitrate, nitric acid and acetic anhydride produced mixtures of the powerful explosives HMX and RDX [6]. Mechanisms postulated [3-5,7,8] for these reactions include the selective cleavage of hexamine, or the total cleavage to simple molecules followed by nitration and recombination.

HMX exists in four solid phase polymorphs, labeled α, β, γ, and δ-HMX [9], each of which can be prepared by a specific cooling rate of the reaction solution [10]. The phase conversion of the β phase (monoclinic lattice structure) to the δ phase (hexagonal lattice structure) involves a major disruption of the crystal lattice and a ring conformation change from β (chair) to δ (boat). The electrostatic forces within the HMX lattice produce an energy barrier, characterized by an activation energy, to overcome during the $\beta \rightarrow \delta$ phase transformation [9]. The volume expansion associated with the $\beta \rightarrow \delta$ phase transition is approximately 6.7% (the density is 1.90g/cm^3 for β and 1.78 g/cm^3 for δ) and may produce profound perturbations to the mechanical and combustion characteristics of HMX [9]. The higher density material shows a higher rate of detonation and maintains greater stability towards shock. Sensitivity to impact [11] has been investigated for safety of handling and long-term storage. β-HMX has a recorded height of sensitivity to impact of 31-32 cm, while δ HMX has a recorded height of sensitivity to impact of 6-12 cm.

Therefore, the mechanical, thermodynamic, and kinetic information associated with the β→δ solid phase transition is of interest to manufactures and handlers of these types of materials. Textbook and literature values are useful to experimenters but are often given as singular values at ambient temperatures and pressures. Information such as this does not always suffice for experiments such as thermal cook-off, where a dynamic temperature/pressure range is involved.

The current lack of consensus on the kinetics of the β→δ solid-solid phase transition is largely due to the difficulty of measuring solid transitions [12]. This work is a step towards building that consensus by determining CTE values by thermo-mechanical analysis (TMA) over a dynamic temperature range for both the β and δ phases, measuring the coefficient of thermal expansion (CTE) during the HMX transition from β phase to δ phase, and quantitatively comparing the rate of dimensional change with a kinetic model calibrated by differential scanning calorimetry (DSC). We also report an indirect measurement δ→β back conversion by both TMA and DSC.

2 Experimental methods

2.1 Samples

Two lots of HMX material manufactured by Holsten Corporation were used: B-844 (HOL 81HO30-033, class A) and A-567 (HOL-704-6 Batch 6HCD-141, Class D). HMX lot B-844 was 99% pure as measured by HPLC. The average particle size was 160 μm, with the central 80% being between 30 and 300 μm. HMX lot A-567 was used as received.

Lot A-567 appeared to have some particle conglomerates that were approximately 250-400 μm in diameter. Both materials were used as powders for DSC experiments. TMA samples used lot B-844 only and were uniaxially pressed at room temperature from dry powder into a right cylinder. A compaction die using a hydraulic press and a single pressing cycle of 10,000 psi to the sample dimensions of approximately 4.5 mm length and 6.3 mm in diameter (nominal mass of ≤0.250 g).

2.2 TMA Measurements

Thermo-mechanical analysis (TMA) is a well-known technique [13] that measures linear or volumetric changes as a function of time, temperature and force. Collected thermal data can provide information and a better understanding of physical properties with respect to time, temperature and heat flow, i.e. glass transitions, solid-solid phase transition, softening point, to name a few. TMA provides basic information of expansion coefficient, transition onset, inflection point, and step transition temperatures and time. Programmed cyclic thermal heating and cooling profiles have been used by Kolb [14] and Maienschein [15] in an effort to better understand the effects that thermal conditions produce with compounds that incorporate binders and energetic materials [16].

A TA Instruments (New Castle, Delaware) Model 2940 TMA controlled by a TA 500 Thermal Analyzer was used in the compression mode for all TMA measurements. A mechanical cooling accessory, manufactured by TA Instruments, controlled the temperature. A quartz micro-expansion probe with a force of 0.01 Newtons (N) was used for all samples. Ultra-high-purity nitrogen carrier gas was used at a constant flow rate of 100 cm^3/min. Samples were heated at a linear heating rate of 3°C/min.

Temperature, force, probe and cell constant calibrations were carried out as outlined [17]. Indium, tin, lead and zinc metals were used for temperature calibration of the instrument. Coefficient of thermal expansion, CTE, measurements using a certified aluminum standard had less than ± 2 % errors associated over the manufacturer's suggested temperature range of –47˚C to 147˚C.

2.3 DSC Measurements

DSC measures the difference in the heat flow between a sample and an inert reference as a function of time and temperature. Both the sample and reference are subjected to a controlled environment of time, temperature, and pressure. A linear change of temperature with respect to time is the customary method of operation for DSC, with ramp rates up to 100 °C/min possible. The instrument design used for making DSC measurements in this work is the heat flux design, TA Instruments Model 2920 [13].

The DSC was calibrated at a ramp rate of 10˚C/min for temperature and heat flow and to reduce baseline drift. Indium, lead, tin, and zinc were used for temperature calibration, and the indium heat of fusion was used for heat flow calibration. The instrumental error was ≤ 1.4°C in temperature and ≤ 2.0% in heat flow—typical for this type of measurement.

DSC data were recorded at linear heating rates of 0.5, 1.0 and 10 °C/min using sample masses of about 0.5-1.0 mg. The thermal ramp was extended to a temperature sufficient to bring the phase conversion to completion, but it was stopped below the temperature where HMX decomposes exothermically. The lids of the DSC sample pans were perforated to maintain the sample at atmospheric pressure. All data are reported with endotherm down.

3 Results

3.1 TMA Measurements

The initial dimensions of the cylinders used in the TMA measurements are given in Table 1. The initial pressing achieved 92-93% of the theoretical maximum density (TMD) [18]. After the first heating and storage of sample T01-843 for 3 days at room temperature, the cylinder volume had increased by 12.7%, with a corresponding increase in porosity. The mass decreased by 0.4%, which could be due to moisture or occluded solvent loss.

Figure 1 shows the dimensional change versus temperature for two HMX samples heated twice at 3˚C/min through the β→δ phase transition. The first heating had an upper limit of 215˚C. Next, the samples were cooled at the same rate to a temperature of 50˚C, and then immediately heated a second time to 215˚C at 3˚C/min. The β→δ phase transition is evident during first heating between approximately 185˚C and 200˚C. No phase transition is evident during the second heating.

Figure 2 shows the dimensional change versus temperature for another HMX sample heated three times through the phase transition temperature. The β→δ phase transformation is clearly observable during the first heating. After the first heating, the sample sat for three days at ambient temperature and pressure prior to being heated a second time. A smaller linear dimensional change is observed (1.65% vs. 5.48%), suggesting that at least partial back conversion to the β phase had occurred during the three days. The sample was immediately cooled to room temperature and then heated a third time through the transition temperature. As in Figure 1, no phase transition is evident this time.

It has been observed in previous work [19] that rapid cooling can cause the HMX delta phase to be trapped even when the temperatures go well below the transition temperature. We believe based on literature information [19,20,21] that the second heating in Figure 1 and the third heating in Figure 2 yield the CTE of δ phase HMX. The CTE values are tabulated for sample T01-843 in Table 2 and for samples T04-511 and T04-516 in Table 3.

Inflection points of the $\beta \rightarrow \delta$ phase transitions during the first two heat cycles were derived from the first derivative of the dimensional change with respect to temperature. The temperatures were found to be 178.2˚C for the first heat cycle and 185.0˚C for the second heat cycle. This shift of 7˚C for the second heat cycle indicates that the back-converted material has greater thermal stability than the original material. The CTE for the δ phase (above 175˚C) is smaller in the first cycle, possibly due to experimental error.

The dimensional change for each sample is given in Table 4. Linear growth during the first heat cycle (T01-843) was 0.0302 cm, or 6.87%, at 215˚C. From Figure 2, ~80% of that growth occurs during the phase transition, which implies a 17% volumetric increase during the transition, assuming isotropic expansion. This is greater than the 6.7% density difference for full-density material and suggests that significant porosity has been created—consistent with previous observations [16,17]. Since sample T01-843 was not measured immediately after cooling, the linear contraction was estimated from other experiments as -0.004 cm (~0.9%). After three days, the sample was 0.472 cm, which is 0.0210 cm (~4.7%) greater than the initial value. This indicates shrinkage of 2.2% during cooling and storage, of which about 1.3% might be attributed to back conversion. The observed expansion after the second heat cycle was 0.0110 cm, and ~0.080 cm of that occurs during the phase transition. The ratio of phase-transition expansions during the second and first heating suggests that at least 32% back conversion occurred. Because the reverted material is more porous, even fully reverted material might expand less during a second transformation.

3.2 DSC Measurements

Two back-to-back DSC thermal scans were carried out using HMX lot A-567, shown in Figure 3. The sample consisted of one large piece of HMX, a conglomerate made up of many smaller particles, and was analyzed using a linear heating rate of 10˚C/min from room temperature to 210˚C. After the first heating the sample was quickly cooled to room temperature over approximately 10 min, then re-heated from room temperature to 210˚C a second time at 10˚C/min. No endotherm is observed during the second heating, supporting other evidence that the phase transition does not occur during a rapid temperature quench [19].

A second DSC experiment, shown in Figure 4, heated a single conglomerate sample at 0.5˚C/min to approximately 200˚C, held it there for two minutes to ensure that the β → δ solid-solid phase conversion was complete, and then cooled it down at 0.5˚C/min to approximately 50˚C. No sharp exotherm or endotherm is observed (Figure 4). A slight depression of the heat flow signal is observed between approximately 155˚C and 190˚C. This could, in principle, be the gradual back conversion from the δ →β solid phase. The back conversion from the δ →β solid phase has been studied previously [20], and it is difficult to observe [21, 22].

Figure 5 shows an expanded view of the first and second endotherms of HMX lots B-844 and A-567 after being stored at room temperature for one and three days, respectively. The peak temperatures of the initial endotherm were ~198˚C and 179˚C, respectively, and about half the difference can be attributed to the faster heating rate for Lot B-844. The first endotherm for Lot B-844 shows jagged regions (fine structure) due to the solid-solid phase conversion of the individual HMX crystals. The second endotherm has less fine structure a lower peak temperature of ~192˚C–approximately 6˚C lower than for the first heat cycle. HMX lot A-567 shows less fine structure than virgin B-844 in the first heating endotherm. The second heating endotherm peak temperature is observed at ~187˚C. Essentially all of the difference in peak temperature of the second endotherms of the two samples can be attributed to the difference in heating rate.

A similar experiment using a single crystal of HMX was reported earlier by Burnham et al. [23] In this case, the first heating produces a single sharp endotherm while the second heating after five days produces a broader, higher-temperature endotherm similar to that from the second heating of the polycrystalline sample. In all three cases, the second endotherm reflects a more homogeneous, finely polycrystalline material, which can transform at higher or lower temperature than the original endotherm, depending on the nature of the virgin material.

The enthalpy in each of these three cases (24-28 J/g) is less than for the virgin material. We initially assumed this meant back-conversion was not yet complete. Consequently, we conducted another series of experiments using lot B-844 in which the endotherm during a second heating was measured after being held at room temperature for various times in order to measure the back conversion kinetics more precisely. As in Figure 5, the reheat endotherm after 5 days, shown in Figure 6, is smoother than that of the original heating, and the enthalpy of 27 J/g is within the range of the earlier experiments.

More interesting, as shown in Figure 7, is that this value appears to be a plateau in enthalpy recovery that starts after a couple hours at room temperature and reaches half the plateau value in 8 hours. From these results, the back conversion appears essentially complete after one day, and the lower ultimate enthalpy is probably due to a very defective crystal structure in the reverted material. In parallel to the enthalpy, the peak temperature of the second transition initially rises and reaches a plateau value.

After normalizing the enthalpies from the second heating to the asymptotic value of 26.5 J/g, the fraction back converted to β phase was fitted to an extended Prout-Tompkins nucleation-growth model [24]:

$$d\alpha/dt = k(1-\alpha)^n(1-q(1-\alpha))^m \qquad (1)$$

where α is the fraction back converted, n is the reaction order, q is an initiation parameter, and m is a nucleation-growth parameter. The results of this fit are shown in Figure 8. The back-conversion has a fairly long induction time, which requires a value of q very close to one.

4 Discussion

Brill et al. [20] have carried out in-depth FTIR experiments on the β→δ solid-solid phase transition kinetics of HMX in an effort to try and understand the fundamental inter-conversions of the polymorphic phases. Weese et al. [25] discussed methods for measuring the transition by DSC. Smilowitz et al. [19] discussed how controlled cooling of HMX could be used to kinetically trap the δ-phase nitramine. Both Henson et al. [26] and Burnham et al. [23] have presented kinetic models incorporating back-reaction.

Both the TMA and DSC results reported here are consistent with earlier work. Forward conversion is easily observed by both methods in the 180-200 ^{o}C temperature region. The unconstrained volume increase during the transition as measured by the TMA is ~15%. This is greater than the theoretical minimum of 6.7% based on single crystal densities and is undoubtedly due to induced porosity, which is readily visible in optical movies of single crystal transformations [23].

The $\beta \rightarrow \delta$ transformation measured by TMA is compared quantitatively in Figure 7 with model predictions using the thermodynamically inhibited nucleation-growth kinetic model of Burnham et al. [23], in which equation (1) is modified by the factor (1-1/K), where K is the phase-transition equilibrium constant. The calculated dimensional change includes the thermal expansions of both phases in addition to the phase transition itself. Due to differences in initial length for the two experiments, the increase in both experiments is normalized to 200 μm. The agreement is very good. The measurements are also qualitatively consistent with kinetic model of Henson et al. [26].

The ratio of 0.32 for the dimensional expansions during the first and second heating of sample T01-843 probably represents complete back conversion rather than a measure of fractional back conversion as we first thought. The DSC studies indicate that the material completely reverts to β phase in about one day, although the reverted material has only 80% of the original enthalpy, most likely due to the formation of a highly defective crystal structure. Instead, the smaller dimensional increase during the second heating is probably because there is no additional porosity created during the second phase transformation. The original phase transition creates two to three times as much volumetric expansion as required for the full density material transformation, while the second transformation causes a volumetric increase approximately equal to the ideal value.

In addition to agreement with previous work on these aspects, we report here the first detailed measurements by this method, to our knowledge, of the CTE of the δ phase of HMX. The δ-phase measurements were collected on rapidly quenched samples, which showed no transition endotherm when reheated. The temperature dependencies of the CTEs are markedly different for the β and δ phases. The β-phase CTE increases from ~37 μm/m˚C near room temperature to 80-100 μm/m˚C at 80, with minor increases up to the phase transition. The δ-phase CTE is more nearly constant in the 50-60 μm/m˚C range.

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6 References

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Table 1. Sample dimensions (cm), masses (g), volumes (cm^3), densities (g/cm^3), and %TMD values.

sample I.D.	heat cycle	length	diameter	mass	volume	density	%TMD
T01-843	1	0.451	0.634	0.249	0.142	1.749	91.81
T01-843	2	0.472	0.656	0.248	0.160	1.559	81.84
T04-511	1	0.354	0.634	0.199	0.112	1.775	93.18
T04-516	1	0.362	0.635	0.199	0.114	1.748	91.76

The reported literature value for the theoretical maximum density of HMX [18] is 1.905 g/cm^3.

Table 2. Calculated CTE values, α, µm/m˚C, of HMX from 0˚C to 200˚C (T01-843).

Heating cycle	0˚-25˚C	25˚C-50˚C	50˚C-75˚C	75˚C-100˚C	100˚C-125˚C	125˚C-150˚C	150˚C-175˚C	175˚C-200˚C (2)
1st heat	37	57	76	97	103	100	95 (3)	10 (4)
2nd heat	51	55	62	61	64	55	(1)	66 (5)
3rd heat (2)	50	57	61	58	63	59	53	48

(1) β→δ solid-solid phase transition in this region

(2) δ-phase CTE values

(3) actual temperature range of 150.10˚C to 167.27˚C

(4) actual temperature range of 191.67˚C to 199.99˚C

(5) actual temperature range of 193.47˚C to 199.79˚C

Table 3. CTE values, µm/m•˚C, for HMX from the first and second heating as a function of temperature.

Temperature/ Sample I.D.	Heating cycle	60 to 80˚C	80 to 100˚C	100 to 120˚C	120 to 140˚C	140 to 160˚C	160 to 180˚C	180 to 200˚C	200 to 215˚C (*)
CTE T04-511	1st	72	80	85	88	94	98	-	30
	2nd	53	54	57	58	63	63	65	64
CTE T04-516	1st	69	77	81	85	90	92	-	28
	2nd	50	50	52	54	56	59	57	50

(*) delta phase

Table 4. Sample I.D., number of heat cycles, initial sample length (mm), final sample length (mm), and the calculated volumetric expansions in the axial direction observed by TMA.

Sample I.D.	Heat cycle	Initial length	Final length	% dimensional change
T01-843	1	0.451	0.482	6.87
T01-843	2	0.472	0.486	2.97
T04-511	1	0.354	0.374	5.72
T04-516	1	0.360	0.383	5.88

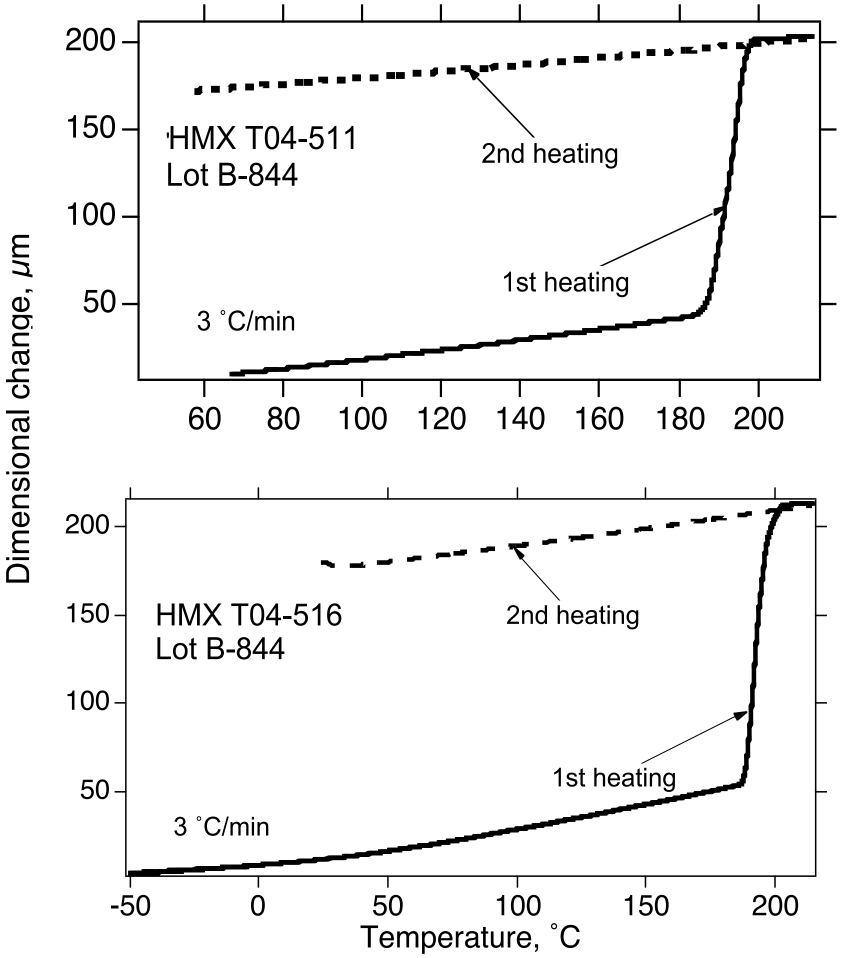

Figure 1. Dimensional change versus temperature during two heating cycles of HMX cylinders T04-511 and T04-516.

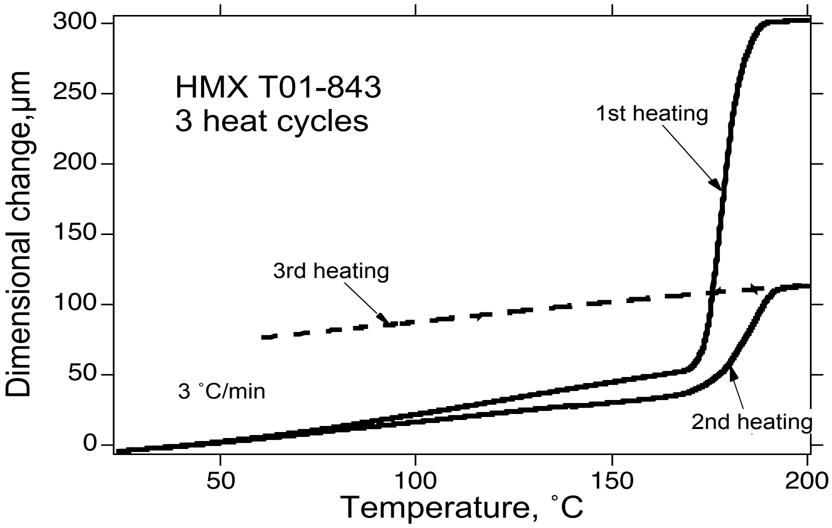

Figure 2. Dimensional change versus temperature for three heating cycles of HMX cylinder T01-843m at a heating rate of 3 °C/min. The first and second heating show a dimensional change due to the β to δ phase transition. The third heating gives expansion of the δ phase.

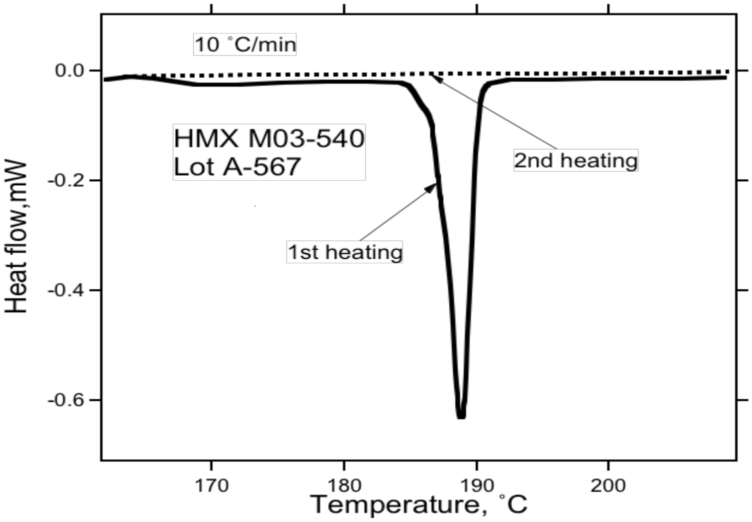

Figure 3. Heat flow versus temperature of two back-to-back heating cycles at 10˚C/min of lot A-567.

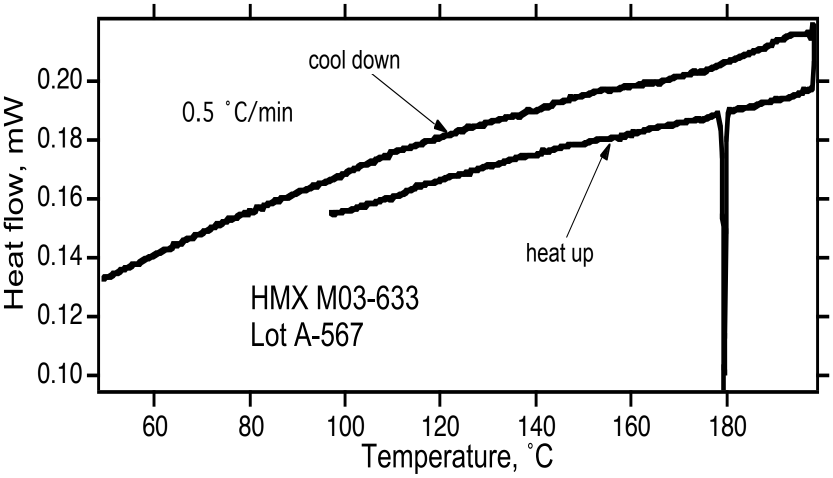

Figure 4. Heat flow versus temperature during heat up and cool down at 0.5˚C/min. The lack of an apparent exotherm suggests no back-conversion occurred.

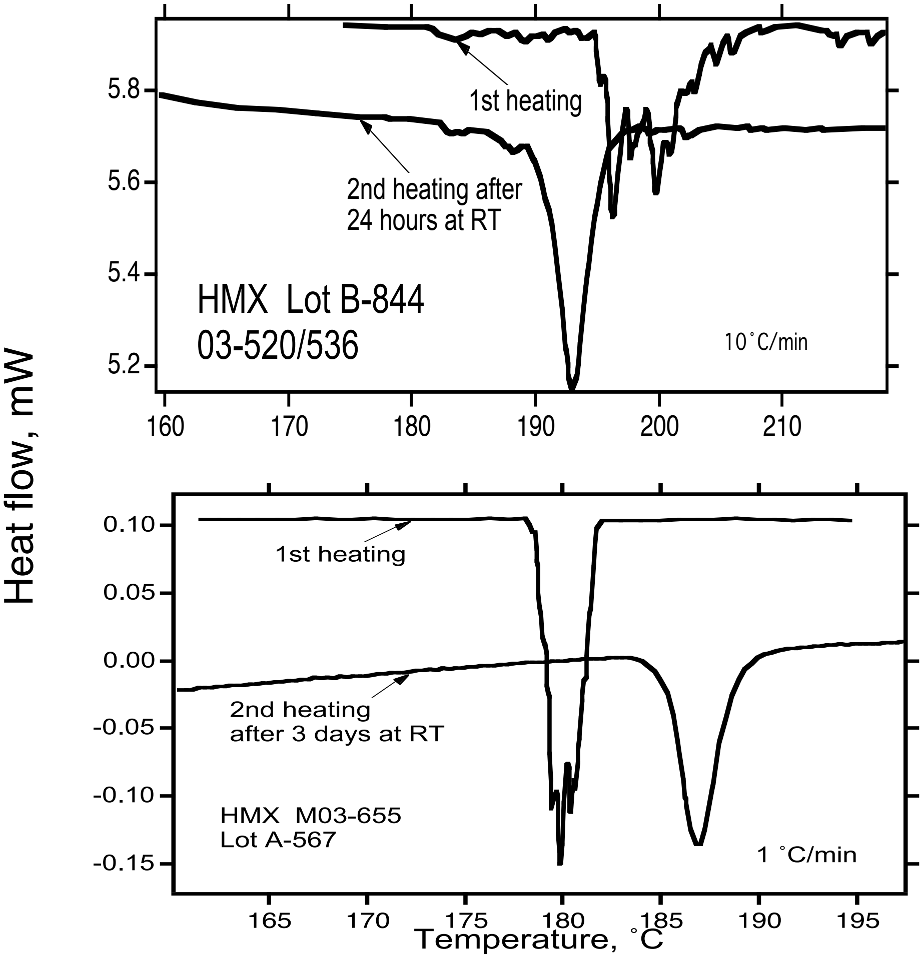

Figure 5. Heat flow versus temperature for two heating cycles of HMX lots B-844 and A-547 at 10 and 1 ^{o}C/min, respectively.

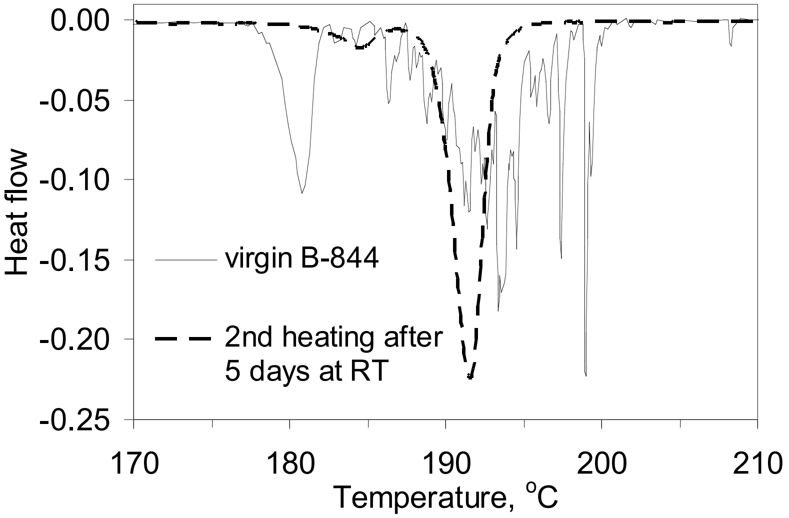

Figure 6. Heat flow versus temperature for two heating cycles of HMX at 3 °C/min.

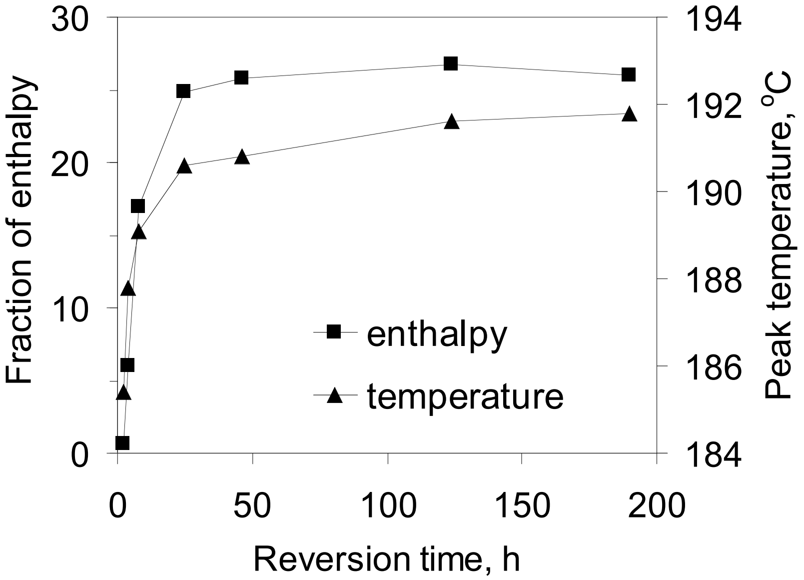

Figure 7. Dependence of the enthalpy from a second heating and the peak temperature of the endotherm on the time at room temperature after the initial heating to convert the material to the δ phase.

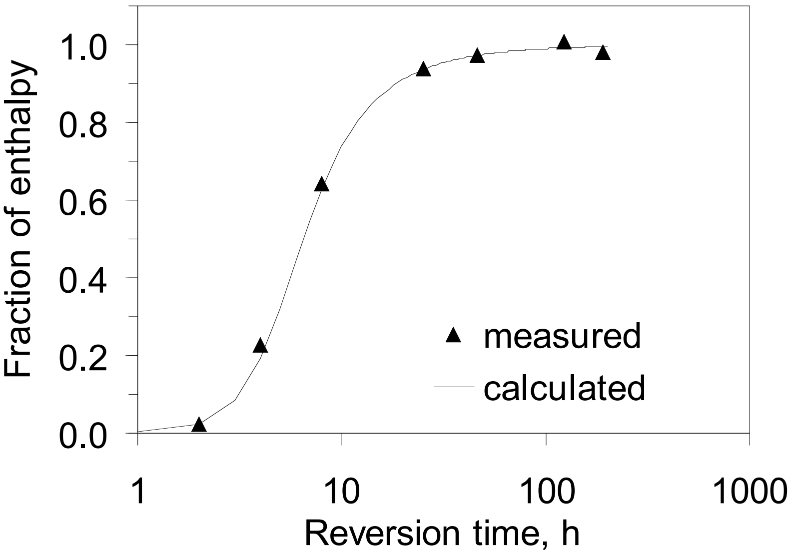

Figure 8. Comparison of measured and calculated fractions of the asymptotic enthalpy as a function of time at room temperature after an initial heating. The kinetic parameters are $k=0.61\ h^{-1}$, $n=1.844$, $q=0.99999$, and $m=0.734$.

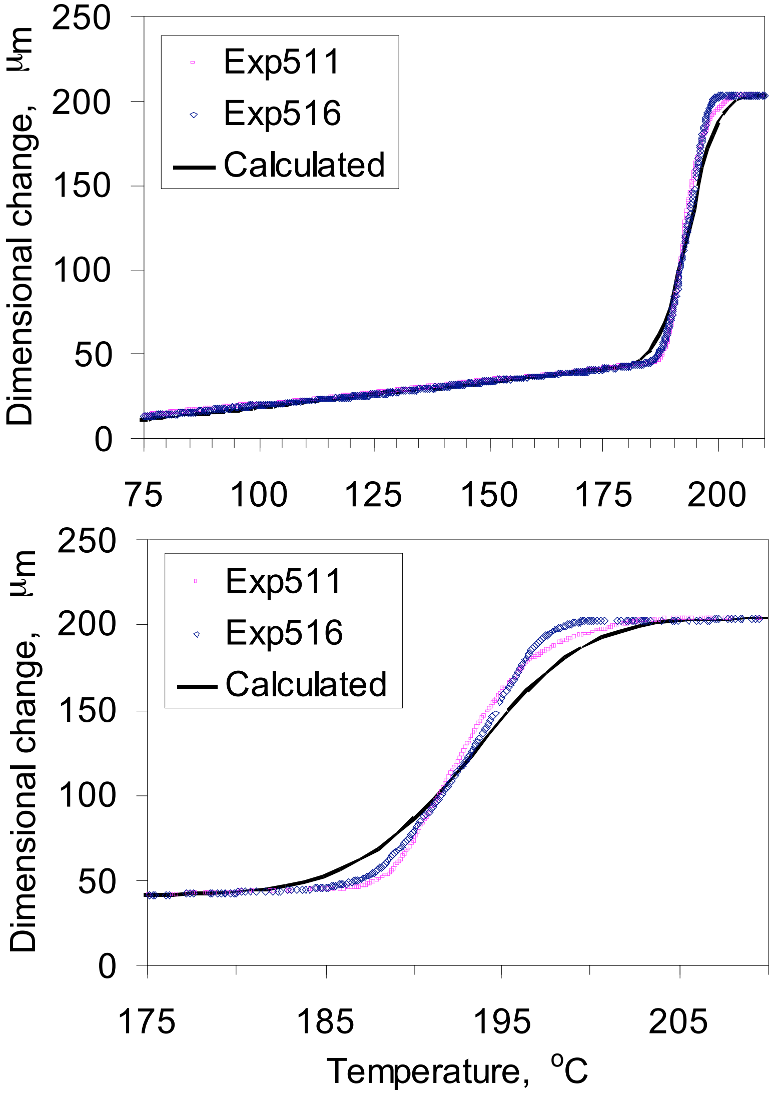

Figure 9. Comparison of measured and calculated dimensional changes using the thermodynamically inhibited, nucleation-growth kinetic model of Burnham et al. [23]: $A=2.91\times10^{22}$, $E=208.8$ kJ/mol, $m=0.18$, $n=1.17$, and $K=13.8\exp(-1182.7/T)$. The comparison is normalized to 200-μm change to eliminate differences due to initial sample size.