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Kinetics of the β→δ Solid-Solid Phase Transition of HMX, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

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Kinetics of the β→δ Solid-Solid Phase Transition of HMX, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

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We apply Differential Scanning Calorimetry, DSC, to measure the kinetics of the β→δ solid-solid phase transition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, HMX. Integration of the DSC signal gives a direct measurement of degree of conversion. We apply 1st order kinetics, the Ozawa method, and isoconversional analysis to show that the phase transition is not a simple one-step reaction, but instead is a complex combination of steps. The range of activation energies found in this work, centering around 500 kJ/mol, is higher than previously reported values. We discuss possible reasons for the higher activation energies measured here.

INTRODUCTION

The chemical compound Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, HMX, is an high-performance nitramine energetic material. HMX exists in four solid phase polymorphs, labeled α, β, γ, δ-HMX, [1, 2] each of which can reportedly be prepared by a specific cooling rate of a reaction solution.[3] The β phase of HMX has the highest density and is stable at room temperature, and is the form in which HMX is normally produced and used. However, when heated to temperatures above 435K, the β-phase converts to δ-phase HMX.[1, 4-7]

This conversion of the β phase (monoclinic lattice structure) to the δ phase (hexagonal lattice structure) involves a major disruption of the cohesive forces in the HMX crystal lattice and a ring conformation change from β (chair) to δ (chair-chair).[8, 9] The electrostatic forces created within the HMX lattice produce a potential energy barrier to overcome in the transformation from the β →δ phase.[5] The energy to bring about the change from chair to chair-chair conformation has been reported by Brill[9] as ring torsion and is essentially a normal mode of the molecule that requires about 4 kJ mol-1. The magnitude of this transformation barrier is indicated by the activation energy of the phase conversion.

The β and δ phases of HMX have quite different behaviors. For example, the volume expansion associated with the β →δ phase transition (the density is 1.90g/cm^3 for β and 1.78 g/cm^3 for δ) produces profound perturbations to the mechanical and combustion characteristics of HMX. [4, 5, 10, 11] The higher density material shows a higher rate of detonation and maintains greater stability towards shock. In sensitivity to mechanical impact as assessed by a standard dropweight impact test such as described by Dobratz,[12] δ-phase HMX is significantly more sensitive than β-phase HMX.[1, 10] It is therefore desirable to know the kinetic information associated with this β → δ solid phase transition. Data have been reported by Brill[5, 13, 14] and by Henson[15, 16] using FTIR and second harmonic generation, respectively, to monitor the transition extent. Here we investigate the kinetics of the β → δ solid phase transition in HMX using Differential Scanning Calorimetry, DSC, and determine kinetic rate parameters and an effective activation energy.

EXPERIMENT

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, shown in Figure 1.

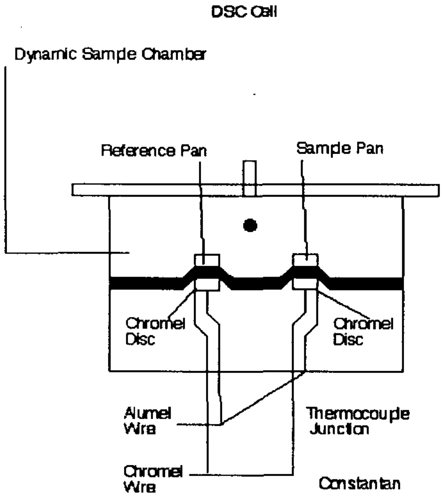

Figure 1: TA Instrument DSC Cell Model 2920 [17]

In this design, a metallic alloy disk, made of constantan, is the primary means of heat transfer to and from the sample and reference.[17] The sample is contained in a metal pan; it and the reference (an empty metal pan of the same composition as the sample pan) both sit on raised platforms formed in the constantan disc. As heat is transferred through the disc, the differential heat flow between the sample and reference is measured by area thermocouples formed by the junction of the constantan disc and chromel wafers, which cover the underside of the platforms. Chromel and alumel wires attach to the chromel wafers and form thermocouples, which directly measures the voltage difference between the sample and reference and converts to temperature.

The DSC was calibrated at each ramp rate 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.

We recorded DSC data at heating rates of 1, 2, 5, and 10°C/m, with sample masses of about 1 mg. The thermal ramp was extended to a temperature sufficient to bring the phase conversion to completion, but was stopped below the temperature where the HMX would exothermically react. We made four runs at each heating rate. The lids of the DSC sample pans were perforated, to maintain the sample at atmospheric pressure.

The HMX used in these experiments was recrystallized from standard-grade HMX, and was 99% pure. The average particle size was 160 micron, and the sample masses ranged from 0.81 – 1.29 mg, with most around 1.1 mg.

RESULTS AND DISCUSSION

The $\beta \rightarrow \delta$ transition in HMX is endothermic, and is readily measured by DSC. Typical data are shown in Figures 2-5 for the different heating rates.

The data in Fig. 2-5 have significant fine structure superimposed on the main thermal event, particularly at the lower heating rates. We conjecture that this is due to uneven contact of the powdered sample with the sample pan, with resulting variations in thermal contact efficiency and therefore heat flow. This would be expected from the change in crystal morphology and density during the phase transition, with different particles undergoing transition at slightly different times and thereby adding a random structure to the overall thermal signature. The presence of this fine structure does not preclude kinetic analysis of the data, however.

The DSC data can be converted to fractional conversion by:

$$\alpha_t = {}^{\Delta H_t}\!/_{\Delta H_{tot}} \qquad (2)$$

where: α_t is the reaction extent at time t

ΔH_t is the total heat of reaction at time t, calculated by integrating the DSC signal up to time t.

ΔH_{tot} is the total heat of reaction, calculated by integrating the DSC signal over the entire phase transition.

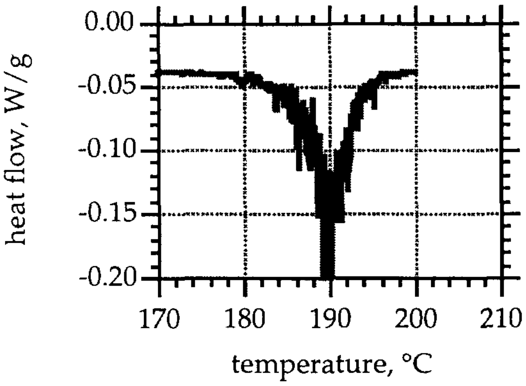

Figure 2. DSC data for 1°C/min. heating rate, #99-896.01

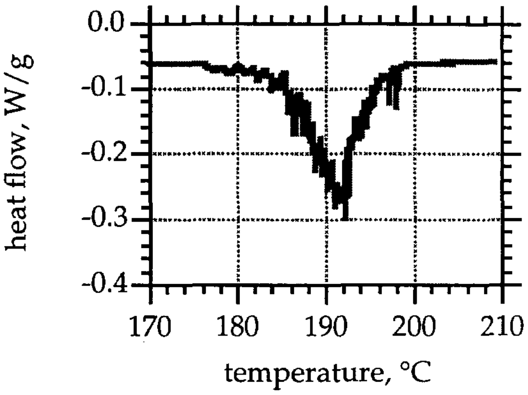

Figure 3. DSC data for 2°C/min. heating rate, #99-890.01

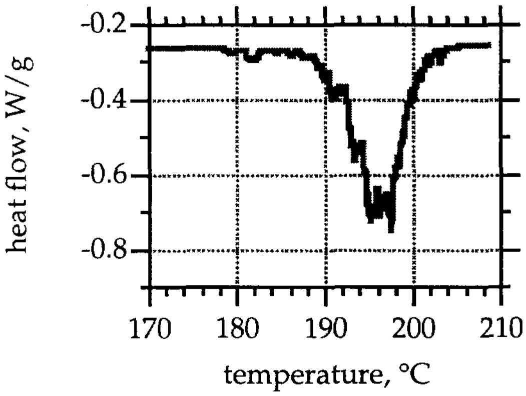

Figure 4. DSC data for 5°C/min. heating rate, #99-878.01

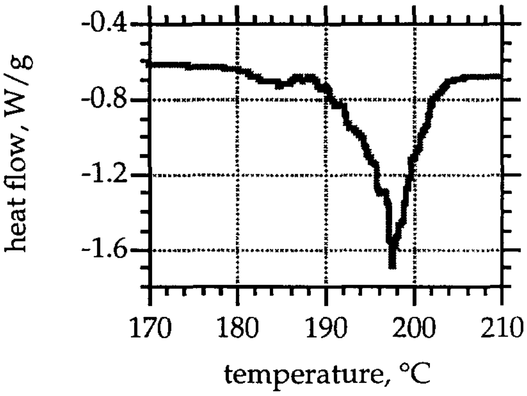

Figure 5. DSC data for 10°C/min. heating rate, #99-872.01

The reaction rate can then be written as:

$$d\alpha/dt = \left(d(\Delta H_t)/dt \right) \times \left(1/\Delta H_{tot} \right) = dQ/dt \times \left(1/\Delta H_{tot} \right) \qquad (3)$$

where: dQ/dt is the heat flow given by the DSC signal.

Calculation of Arrhenius parameters – 1^{st} order assumption

The reaction rate may also be written, for a simple reaction with Arrhenius kinetics, as:

$$d\alpha/dt = k(1-\alpha)^n = Ae^{-E_A/RT}(1-\alpha)^n \qquad (4)$$

where: k = reaction rate constant, s^{-1}
A is the Arrhenius pre-exponential, s^{-1}
E_A is the activation energy, kJ/mol
n is the reaction order.

Combining Eqs.(3) and (4), we can calculate the rate constant as a function of temperature for a given DSC run by:

$$k = {}^{dQ}\!/_{dt} \times \left({}^{1}\!/_{\Delta H_{tot}} \right) \times (1-\alpha)^{-n} \tag{5}$$

We analyzed each DSC run in the following way. First, we integrated the total phase transition signal to determine the total heat of reaction. Then, the reaction extent as a function of time was calculated using Eq.(2). Finally, the reaction rate constant was calculated as a function of time for reaction extents from 20-80% using Eq.(5), assuming first order kinetics. A representative plot of the rate constant as a function of time for one run is shown in Figure 6. For each run, we calculated an average rate constant for reaction extent from 20 to 80%, and using these values we calculated a mean value were calculated for each thermal ramp rate. These mean values are shown in Table 1, and plotted in Figure 7. The resulting activation energy is 433±13 kJ/mol, and the pre-exponential term is $2x10^{48}$ s^{-1}.

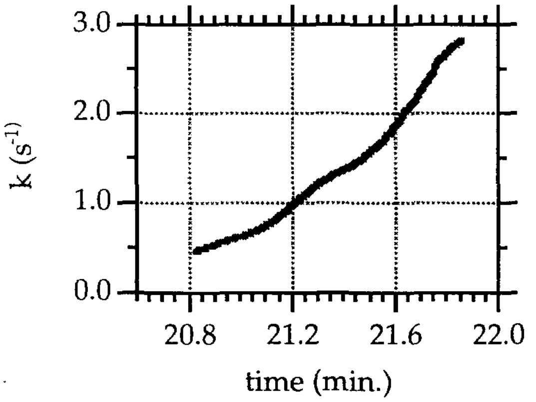

Figure 6. Rate constant calculated from Eq.(5) for run 878.01 at 5°C/min.

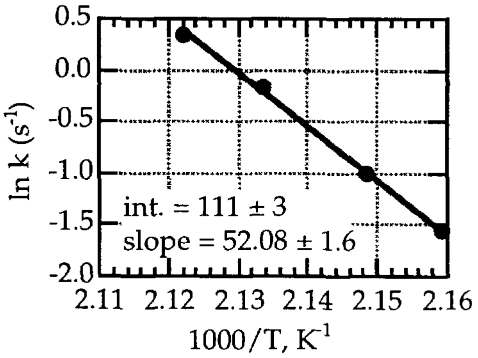

Figure 7. Arrhenius plot of kinetic data from Table 1. Activation energy is 433 kJ/mol, and the pre-exponential term is $2x10^{48}$ s^{-1}.

From Fig.(6), we see that the rate constant during a DSC run is not actually constant. This could be due to a couple of effects. First, the temperature is not constant during the course of the run, so the rate constant would be expected to change. The data in Fig.(6) span about 1 minute or 5 K. Applying the activation energy of 433 kJ/mol to the minimum and maximum temperatures represented in Fig.(6), 466.2 – 471.2 K, we calculate that the rate constant should vary by a factor of 3.3. This is a significant portion of the overall variation of a factor of 6.5, but does not account for all of the variation. Second, a changing rate constant may indicate that the reaction is not as simple as assumed. We assumed a single first order reaction mechanism in this analysis; zero and second order kinetics also yielded a varying rate constant. It is also possible that the reaction has multiple steps or competing processes, in which case this analysis would not give an invariant rate constant. Our method of using the rate constant at the peak of the endotherm is therefore an approximation, and our kinetic constants calculated in this manner must therefore be considered estimates.

Table 1. Mean rate constants and temperatures for each thermal ramp rate, assuming first order kinetics. Values represent averages of four runs at each ramp rate.

Ramp rate, °C/min	k (s^{-1})	T (K)
1	0.208	463.1
2	0.363	465.4
5	0.843	468.7
10	1.41	471.3

Calculation of Arrhenius parameters – Ozawa method

An alternate method of calculating kinetic parameters is the method of Ozawa, wherein the thermal ramp rate as a function of the peak temperature is used for conventional Arrhenius analysis.[18, 25] This gives directly an estimate of the activation energy. The ramp rate and peak temperature data in Table 1 are shown in Arrhenius form in Figure 8. The activation energy, 510 kJ/mol, is significantly higher than that calculated above from the actual reaction rate data.

Calculation of Arrhenius parameters – isoconversional analysis

The above methods for calculating activation energy assume an unchanging reaction mechanism with 1st order reaction. Similar analyses can be made with different reaction orders which lead to different kinetic parameters; it is often difficult if not impossible to determine which is the appropriate reaction order from this type of analysis.[19] Furthermore, if the reaction mechanism changes during the course of the reaction, the above methods can only give a global average that may not truly represent any of the actual mechanistic steps.

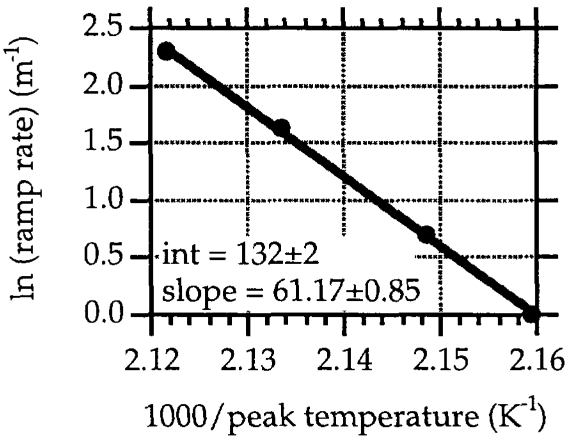

Figure 8. Ramp rate and peak temperature data from Table 1, with a linear fit for calculating activation energy.

Isoconversional analysis is an alternate method of kinetic analysis that avoids these problems.[19-22] In isoconversional analysis, data from several different ramp rates are required. For each ramp rate, the reaction rate and temperature is determined for different extents of reaction; then the Arrhenius parameters are calculated from the set of temperature-rate data at each reaction extent assuming zero-order kinetics (i.e. n=0 in Eq.(4)). Changes in the activation energy with reaction extent indicate changes in reaction mechanisms. The pre-exponential parameter lumps together all reaction-order effects, and so its behavior also may give insight into the actual mechanisms. There is no assumption of reaction order inherent in isoconversional analysis, so the activation energies should be representative of the actual reactions taking place.

Steps in the isoconversional analysis were: 1) calculate the reaction extent from integration of the DSC data, using evenly-spaced temperature data over the same temperature range for each run at given ramp rate; 2) interpolate the temperature / reaction extent data sets to give temperature / reaction extent data at evenly spaced reaction extent values ranging from 0.01 to 0.99; 3) calculate the reaction rate for each reaction extent value from the temperature / reaction extent / ramp rate data; 4) for each reaction extent, use rate/temperature data from the four ramp rates to calculate Arrhenius parameters as a function of reaction extent. Typical results at reaction extents of 0.2 and 0.8 are shown in Figure 9, and the resulting Arrhenius activation energy and pre-exponential values are shown in Figure 10 for reaction extents from 0.05 – 0.95.

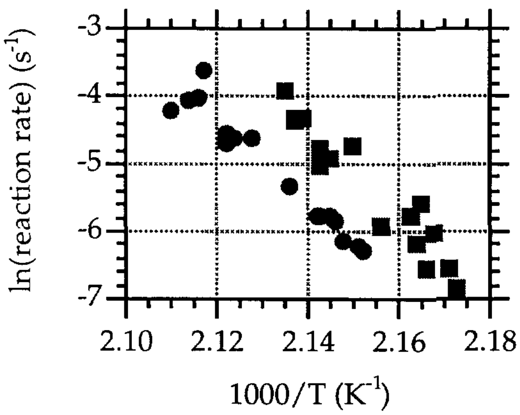

Figure 9. Reaction rates as a function of temperature at reaction extents of 0.2 (square) and 0.8 (circle).

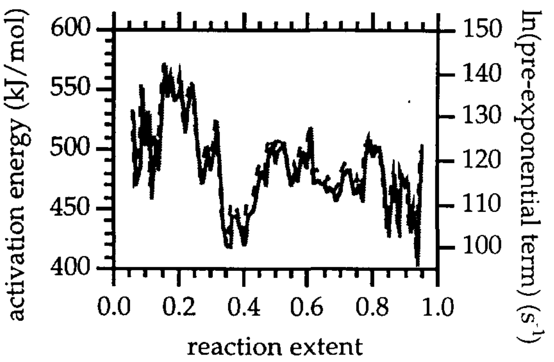

Figure 10. Isoconversional activation energies and pre-exponential values for reaction extents of 0.05 to 0.95.

As we see from Figure 10, there is considerable structure in the Arrhenius parameters as the reaction proceeds, with the activation energy and pre-exponential tracking each other very closely. We can capture most of the features by considering seven regions as defined by reaction extent, and determining an activation energy and pre-exponential value for each region. These values, shown in Table 2 below, were determined from the data in Figure 10, with minor adjustments made as described below in checking the fit of the conversion data to this set of parameters.

Table 2. Arrhenius parameters for the HMX $\beta \rightarrow \delta$ phase transition calculated using isoconversional analysis.

Reaction extent	< 0.15	≤ 0.25	≤ 0.33	≤ 0.47	≤ .63	≤ .81	≤ 1.0
E_A, kJ/mol	481.5	537.5	491.0	465.0	493.0	471.0	479.0
ln (A)	119.0	133.5	122.0	115.0	122.0	116.0	117.0

As a check of the validity of the values in Table 2, we used these parameters to calculate the reaction extent as a function of temperature for the four experimental ramp rates, and then compared the calculated values with the experimental data. This is shown in Figure 11. The agreement is excellent, with the calculated reaction extent fitting well within the envelope of experimental results for each ramp rate. We note that, to achieve the degree of agreement shown in Figure 11, some of the Arrhenius parameters derived from Figure 10 were adjusted to the nearest 0.5 kJ/mol or sec^{-1}. The adjustments were small in all cases, and the adjusted parameters are still consistent with the data shown in Figure 10.

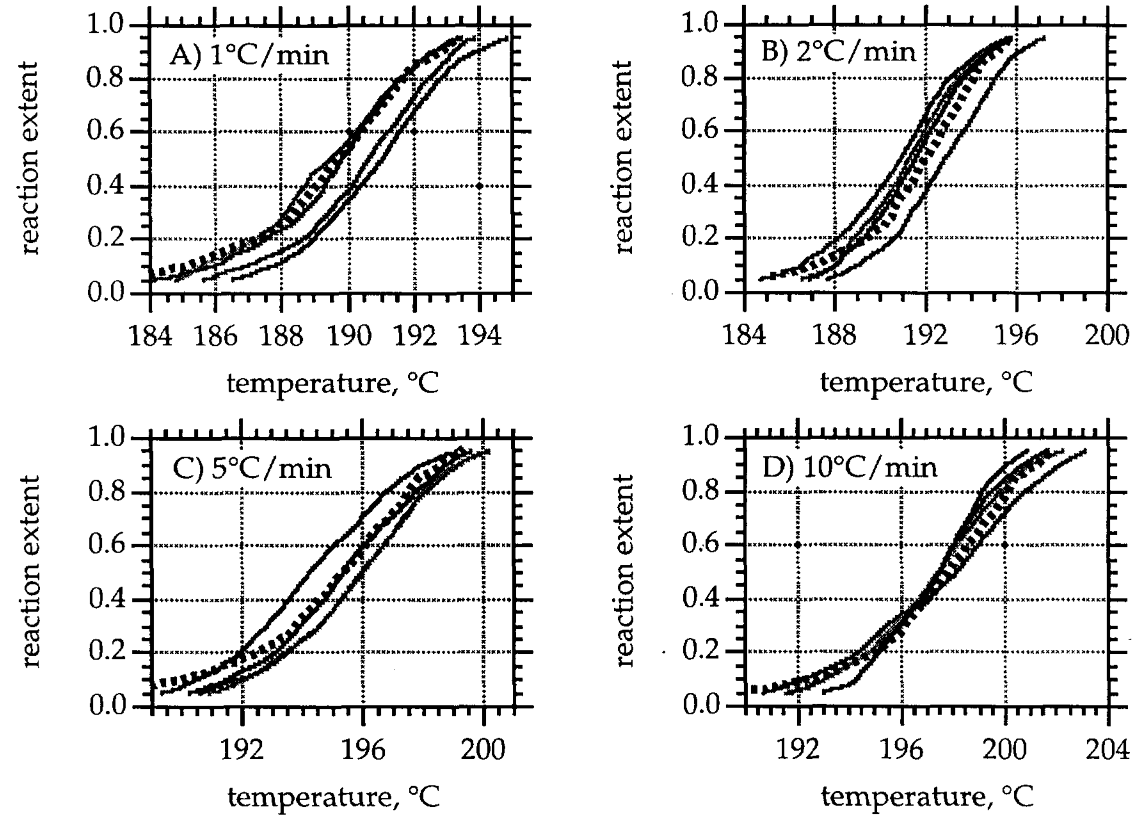

Figure 11. Reaction extent of phase transition. Measured – solid lines. Calculated from Arrhenius parameters in Table 2, thick dotted line. Each plot is for the thermal ramp rate shown on the plot.

From isoconversional analysis results, we conclude that the phase transition kinetics cannot be described by one simple nth order reaction. The range of activation energies at different reaction extents indicates that a more complex set of reactions is taking place. From the data available, we cannot determine a mechanistic scheme, but can deduce that the scheme is not a simple one.

The activation energies for the different steps in the reaction are quite high – 465-538 kJ/mol. These values are consistent with those from our simpler analyses presented earlier – 433 kJ/mol for the 1st order assumption and 510 kJ/mol using the Ozawa method, showing the general validity of the three methods of analysis.

Comparison with literature

With pure HMX and using FTIR spectroscopy to monitor the $\beta \rightarrow \delta$ phase transition, Brill *et al* observed first-order kinetics and determined an activation energy of 204 kJ/mol.[23] Henson *et al* studies HMX mixed with estane and nitroplasticizers (PBX-9501), using second harmonic generation of reflected light to measure the reaction extent.[15, 16, 24] He built a model for the transition based on a nucleation and growth mechanism with a first order nucleation step and a second order growth step; activation energies were on the order of 200 kJ/mol for each step.

Our results show a complex mechanism, which is consistent with Henson's observation that a multi-step reaction mechanism is required to accurately reproduce the experimental results. The range of activation energies that we find, around 500 kJ/mol, are significantly higher than those found by Brill and by Henson. The reasons for this are not fully understood. One difference is the measurement method. Our measurements are the first reported using thermal data to monitor the progress of reaction in bulk HMX samples. DSC measures the reaction progress *in situ* integrated across the entire sample, in contrast to the other techniques. The second harmonic generation method observing reflected light used by Henson monitors the surface of the sample; if the surface and bulk kinetics differ, then a difference in results would be expected. The FTIR method used by Brill samples only the sample area interrogated by the FTIR beam, and requires a very thin sample to transmit the IR signal, essentially a surface sampling technique.

A second possible reason for the difference in activation energies is the composition of the samples. Henson's studies used PBX-9501, a mixture of HMX with estane and nitroplasticizers. Brill's work, while done with pure HMX, required the use of a silicone oil for heat transfer. Our experiments used pure HMX with no binder and no additives. It is plausible that the presence of such additives would alter the kinetics of the phase conversion, and we have work underway to study that hypothesis.

CONCLUSIONS

We have monitored the reaction progress of the HMX $\beta \rightarrow \delta$ phase transition using differential scanning calorimetry and pure HMX, and analyzed the results using three methods – assuming 1st order kinetics, the Ozawa method, and isoconversional analysis. Isoconversional analysis shows that the reaction mechanism is not a simple one-step reaction, but instead involves multiple reaction steps; analyses using simple reaction mechanisms must necessarily be approximations that may of limited validity. There are many factors that contribute to an overall reaction mechanism, and our measurements do not define these factors and their relevance, but instead show that such factors are important.

The activation energies with different analytical methods are all around 500 kJ/mol, significantly higher than reported in the literature. As discussed above, this may be the result of other work using experimental methods that monitor surface instead of bulk behaviors, and may also relate to the chemical additives present in many of the samples

ACKNOWLEDGEMENTS

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