

Rapid-Heating of Ionic Energetic Materials using a Micro-Differential Scanning Calorimeter

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Abstract:

A previously developed micro-Differential Scanning Calorimeter (μ -DSC) has been shown to be effective in studying the thermal decomposition of organic energetic materials. Due to its compact size, this device is capable of rapid heating rates and sensitive detection of thermal loads from very small samples. Temperature calibration was done by heating Sn, KNO₃, and KClO₄ at the desired heating rates to determine the temperature profile at each rate. The samples 5-amino-1*H*-tetrazole, 5-amino-1-methyl-1*H*-tetrazolium dinitramide, 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide, and 1,5-diamino-4-methyl-1*H*-tetrazolium azide, were all tested at four heating rates ranging from \sim (1900 to 64,000) K/s. These heating rates are orders of magnitude greater than those used in traditional DSC experiments, and comparison at high and low heating rates shows differences in the thermal signatures. Using the Kissinger method, the activation energy of each material is determined.

Keywords: Differential scanning calorimeter; Tetrazolium salts; Energetic materials

1. Introduction

Differential scanning calorimetry (DSC) is often used as a characterization technique to determine the thermal behavior of energetic materials (EMs). As new organic EMs are formulated, this is an important test to determine thermal stability and ignition temperature. Recently, new organic energetic materials are being created to not only improve performance and stability, but also to reduce their environmental impact. These “green” energetics are generally high-nitrogen content ionic salts which have N₂ gas as a primary reaction product and create the majority of their energy from high heats of formation. Conversely, classic organic explosives (TNT, RDX, etc.) create energy through oxidation of a carbon backbone,[1] which

often results in gaseous carbon containing reaction products.. Many ionic salts have a tetrazole-containing cation, which aids the high-nitrogen content of the material. Two common cation structures are 5-amino-1H-tetrazole, and 1,5-diaminotetrazole which have 82.3 wt.% and 84 wt.% nitrogen respectively,[2] while the anion can be composed of a variety of different structures.

Several groups have characterized high-nitrogen energetics via DSC and related experiments. 5-aminotetrazolium nitrate[3], 1,5-diamino-4-methyl-1*H*-tetrazolium nitrate[4], 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide[4], 1,5-diamino-4-methyl-1*H*-tetrazolium azide[4], and 5-aminotetrazolium dinitramide[5], are just a few examples of ionic salts that have been characterized by standard DSC methods. In addition to decomposition temperature, activation energy can be calculated using varied heating rate experiments and either an iso-conversion technique like that by Ozawa[6] or the Kissinger method[7]. Ma *et al* performed this experiment for 5-aminotetrazolium nitrate from (2 to 25) K/min and obtained an activation energy of 303.2 kJ/mol using the Ozawa method and 311.0 kJ/mol using the Kissinger method.[3] In a similar DSC experiment at heating rates of (2 to 40) K/min, Fischer *et al* determined the activation energy of several ionic salts and found them to be in the range of ~(101 to 138) kJ/mol using both the Ozawa and Kissinger methods.[4] Relative to heating rates commonly experienced during combustion of energetic materials, traditional DSC heating rates are many orders of magnitude lower. This is relevant as higher heating rates may lead to different mechanistic steps in the reaction. For example, it is established that as the heating rate increases, the activation energy tends to decrease. Heating experiments for Ge₂Sb₂Te₅ films showed the activation energy for film crystallization decreased by more than a factor of 4 over a heating rate range of 3–500 K/min.

To achieve very high heating rates that approach those that are relevant to energetic materials, new classes of DSC devices are necessary. These new devices based on MEMS fabrication methods offer very fast response due to the small thermal mass of the heaters and small sample size.[8-11] A μ -DSC device previously developed at the National Institute of Standards and Technology (NIST) is capable of heating rates up to 1×10^7 K/s,[11] and was previously used to explore phase changes in Ni/Si thin films.[12] This device is used to investigate the decomposition temperature and activation energy of several high-nitrogen energetic salts and results are compared with that of traditional DSC.

2. Experimental

The main diagnostic tool in this study is a silicon based μ -DSC device[11] (66 x 240 x 3.3 μ m) shown in Figure 1, where the center rectangular section is the heated platform. The heated platform can be split through the vertical axis into two halves; one holds the sample and the other serves as a reference during heating. Each section has a poly-silicon heater, which is driven by a function generator (Tabor Electronics WS8102)[13] that supplies a linear voltage ramp. An aluminum poly-silicon thermopile consisting of a series of twelve junctions, located sequentially on opposite ends of the device, produces a voltage proportional to the temperature difference between the two sections. Heating rates can be varied by adjusting the frequency of the function generator, and for these experiments the heating rates ranged from \sim (1900 to 64,000) K/s. Samples are placed onto the surface of the μ -DSC using a PV820 Pneumatic Pico-pump system (World Precision Instruments) capable of producing pico-liter sized drops. Droplet size is typically on the order of 10's of micrometers in diameter. The pico-pump works by applying a short (5 ms) pressure burst to the liquid in the micropipette, causing a droplet to be

ejected from the tip. Drop sizes were determined optically from images such as Figure 1 and ranged from $\sim 10 \mu\text{m}$ to $60 \mu\text{m}$ in diameter. Each sample was initially placed in either ethanol or methanol at a concentration of $\sim 100\text{mg/ml}$ to maintain stability of the material. Samples were then diluted with H_2O to a concentration of $\sim 10 \text{mg/ml}$ to prevent drying in the micropipette. The volume of the drop was estimated by assuming that wetting of the surface occurs in a similar fashion to a drop of water on a silicon surface. The contact angle of the drop was taken to be 30° [14] and the curvature of the drop was assumed to be similar to a spherical cap.[15] Assuming the diameter of the drop as viewed in Figure 1 to be $60 \mu\text{m}$ the mass of sample is estimated to be 0.1ng .

All organic energetic materials used in this experiment were provided by T.M. Klapötke of Ludwig-Maximilians University in Munich, Germany. The materials studied were 5-amino-1*H*-tetrazole (5-AT), 5-amino-1-methyl-1*H*-tetrazolium dinitramide (MeHAT_DN), 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide (MeDAT_DN), and 1,5-diamino-4-methyl-1*H*-tetrazolium azide (MeDAT_N3). The synthesis of each material has been documented elsewhere with the exception of 5-aminotetrazole which was acquired from Sigma-Aldrich.[5, 16-18] Aside from 5-AT, these materials are novel energetics and have been recently formulated, therefore a limited amount of diagnostic information is available.

Linear voltage ramps were used to drive the heaters and approximate a linear temperature ramp for the sample. Calibration was performed to confirm the temperature of the heating surface using three samples with well documented phase change points, tin (Sn), potassium perchlorate (KClO_4), and potassium nitrate (KNO_3), which has two calibration points. The known calibration points were the melting point of tin at 505.1K [19], a solid-solid phase transition for KClO_4 at 572K [20], a KNO_3 solid-solid phase transition at 401K [20, 21], and

melting at 607 K [22]. With the known thermal properties of each material, four heating rates are applied, ~1900 K/s, ~6500 K/s, ~33,000 K/s, and ~64,000 K/s. For each material the voltage point at the onset of melting was measured and plotted in Figure 2. A linear function was created to convert voltage to temperature for each heating rate, the results of which are also shown in Figure 2. To achieve a desired temperature and ramp rate, the voltage and ramp duration were determined and applied for each heating rate. Due to the method of calibration, and very small sample sizes, we do not expect thermal lag or sample self-heating to be an issue with this system.

3. Results and Discussion

The decomposition temperature of each material at four different heating rates is shown in Figure 3. In varied heating rate experiments it is possible to extract kinetic parameters using the Kissinger method[7],

$$\ln\left(\frac{\beta_i}{T_{p,i}^2}\right) = \text{constant} - \frac{E_a}{RT_{p,i}} \quad (1)$$

where β is the heating rate, T_p is the temperature where the calorimetric trace peaks, and R is the gas constant. Figure 4 plots the left side of equation (1) versus the inverse of the decomposition temperature for each material so that the slope of the data is proportional to the activation energy. Following the Kissinger method, the decomposition temperature is taken from the peak of the calorimetric trace. Each set of data in Figure 4 demonstrates an acceptable degree of linearity, as they each sample has a correlation coefficient of 0.95 or greater.

As previously mentioned, most of these materials are synthesized by the Klapötke group at Ludwig-Maximilian University of Munich. Aside from synthesis, this group executes a variety of performance tests on these materials; therefore much of the work presented here will

be compared with their slow heating experiments. Since these materials show differences in their dependence on heating rate, each will be discussed separately.

3.1. *MeDAT_DN*

A sample DSC trace for MeDAT_DN displaying a strong exothermic peak is shown in Figure 5a. This is consistent with traditional DSC experiments, which also show a strong exotherm. In this low heating rate study, the decomposition peak shifted from (450 to 488) K for a (2 to 40) K/min heating rate range.[4] Figure 3 shows the variance in temperature of exothermic peak for MeDAT_DN in the high heating rate μ -DSC experiments, which occurs in the range of (558 to 682) K. The elevated decomposition temperature in our experiments is a result of the use of high heating rates. Traditional DSC experiments also indicate a melting point at 358 K. While a sharp endotherm is not observed with the μ -DSC, a shallow broad endotherm is present, and likely represents melting. Through the Kissinger method we calculate the activation energy to be ~ 74 kJ/mol, close to half of the ~ 138 kJ/mol calculated by Fischer et al through both the Ozawa and Kissinger methods.[4]

3.2. *MeDAT_N3*

MeDAT_N3 is reported to show an endothermic peak in the range of (458 to 484) K for various low heating rates, and has a reported melting point of 408 K.[4] In Figure 5b a large endothermic peak is observed for this material, which is consistent with the low heating rate work.[4] With the rapid heating rates in this experiment the peak of the decomposition ranges from (473 to 664) K. Again, using the Kissinger method the activation energy is calculated to be ~ 41 kJ/mol, compared to 107 kJ/mol in the Fischer study. The main difference between the high

and low heating-rate calorimetric traces is that the high heating rate study displays a very broad endotherm, compared to a sharp peak at low heating rate Fischer study. We believe this endotherm is a result of both sublimation and decomposition, which at lower heating rates is observed as two endothermic peaks. Aside from heating rate, the main experimental variation between the Fischer work and the present study is that their experiment was performed in a semi-enclosed container which has a 1 μm hole in the top to release gaseous reaction products, and the present work was done in an open environment. Fischer and co-workers mention that if a completely closed container is used then the two endotherms become one. In our μ -DSC experiment, the heating rate may be at a point that the sublimation and decomposition also occur as one process. In Fischer's previous work the sample showed mass loss at a fairly low temperature of 378 K, however there was no DSC signal at this temperature. The broad endothermic nature of the MeDAT_N3 under high heating rates may be explained if this early mass loss is due to an exothermic event that can be better detected with the sensitivity of the μ -DSC.. Another explanation is evaporation of the sample solution before the energetic material reacts. For this to occur the energetic material would need to dissociate and form a solution with a relatively high vapor pressure. However, we do not expect this to happen as these ionic salts are stable in H_2O and ethanol, and are known to have low vapor pressures.

3.3. 5-AT

5-AT is the one material of this set that is a neutral rather than an ionic material. It is tested here as it is the back bone of the cation species in each of the other EMs. This sample at 10 K/min displayed a decomposition temperature of 480 K and has a melting point of 478 K.[2] The activation energy was also reported to be (136 to 153) kJ/mol using several different iso-

conversion methods at heating rates of (0.63 to 40) K/min. Figure 5c shows a sample μ -DSC trace for 5-AT showing two endotherms, the first of which peaks at just over 473 K that we attribute to melting, and the second we consider to be the decomposition. The melting of 5-AT occurs from (478 to 493) K consistently for all heating rates, but the endothermic peak increases with heating rate in the range of (505 to 624) K. In the Lesnikovich study only one major endotherm is observed during DSC experiments, as at slow heating rates these two processes likely happen rapidly and cannot be distinguished separately. From Figure 4, the activation energy was calculated to be ~ 66 kJ/mol. This activation energy is more than half of that previously reported, but is reasonable considering the significant difference in heating rates in the two experiments.

3.4. *MeHAT_DN*

Traditional DSC traces for *MeHAT_DN* at 5 K/min show an endotherm due to melting starting at 363 K and an exotherm starting at 418 K.[17] In the μ -DSC studies the thermal trace of *MeHAT_DN* in Figure 5d can be broken down into multiple reaction steps. First, a slow endotherm starts shortly after the heating and is similar in nature to the endotherm in *MeDAT_N3* in Figure 5b. Secondly, we observed a sharp endotherm, shown in the boxed region of Figure 5d, which is typically followed by a second endotherm.. The calorimetric trace does vary as at the slowest heating rates the two endotherms may appear as one. At times, the gap between the two endotherms is very sharp and appears to be similar to an exothermic event. For use in the Kissinger method the decomposition temperature is taken from the final endothermic peak. It is assumed that if the calorimetric trace only shows one endothermic peak at slow heating rates, that both mechanistic events are present but indistinguishable. This endothermic

peak occurs in the range of (535 to 757) K and the activation energy for MeHAT_DN is ~44 kJ/mol. No value for the activation energy was found in the literature, but this value is consistent with the other materials in this study.

4. Conclusions

This work has successfully demonstrated the ability of the previously designed μ -DSC to study the thermal decomposition of organic energetic materials. For certain materials this system allowed for the probing of different mechanistic steps than is capable with traditional calorimetry experiments. Due to heating rates that are orders of magnitude higher than those that are typically used for DSC experiments we report activation energies that are considerably lower than those previously reported. With the use of the broad heating rate range that this system is capable of, future studies using this technique could provide further insight into the thermal decomposition mechanisms of organic EMs. Possible studies on one material ranging from very slow heating rates, which are typically used, up to very fast heating rates at the high end of this system's capabilities, could be very insightful into the decomposition mechanisms of these materials.

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Figures:

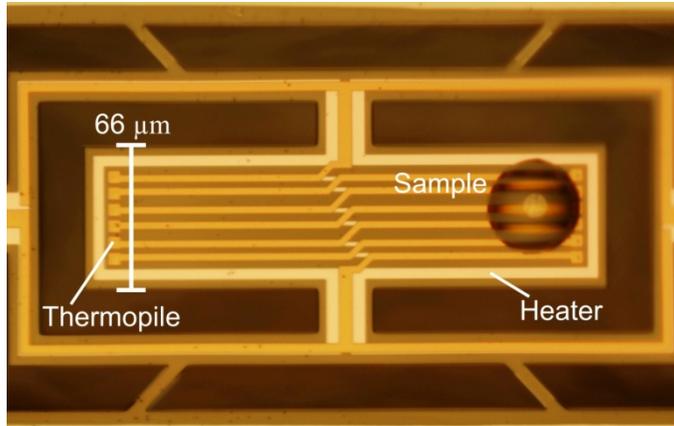


Figure 1: Image of the μ -DSC with a droplet of an organic energetic sample.

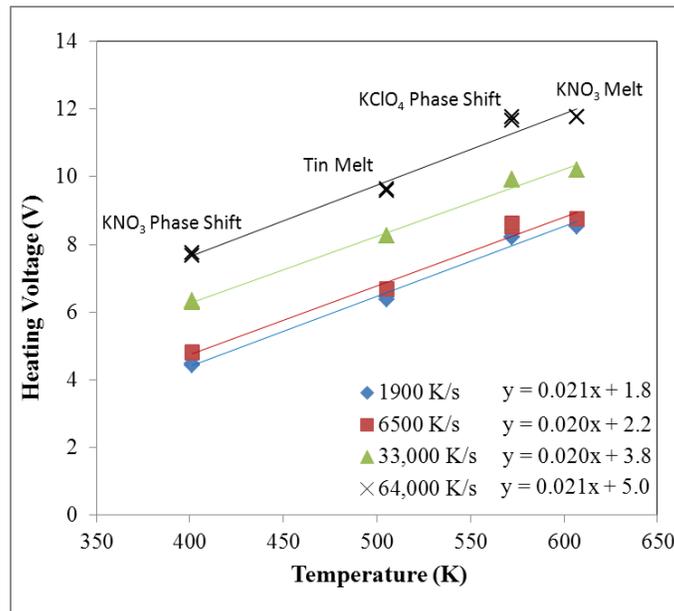


Figure 2: Voltage to temperature calibration for known reference thermal signatures, melting point of tin, 505 K, solid-solid phase transition of KClO_4 , 572.2 K, solid-solid phase transition of KNO_3 , 401.2 K, and melting point of KNO_3 , 607.1 K.

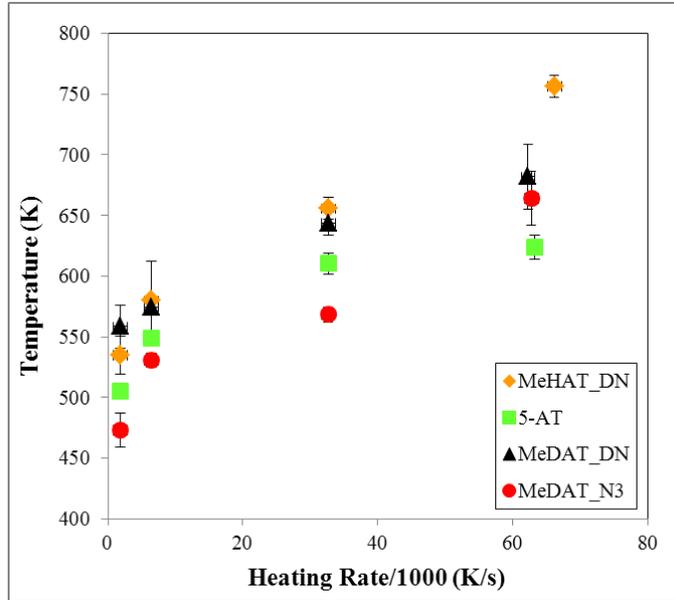


Figure 3: Decomposition temperature of various materials at four different heating rates. Error bars correspond to uncertainty in the assignment of the decomposition temperature due to the breadth of the peak.

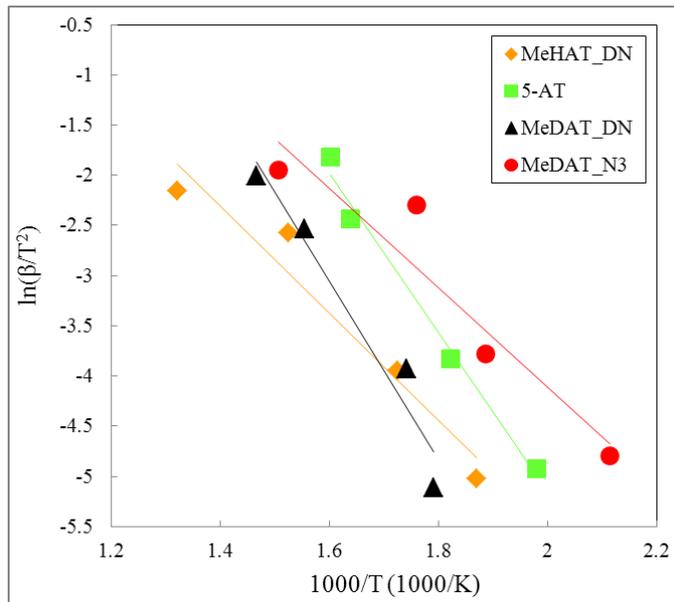


Figure 4: Kissinger plots for each sample.

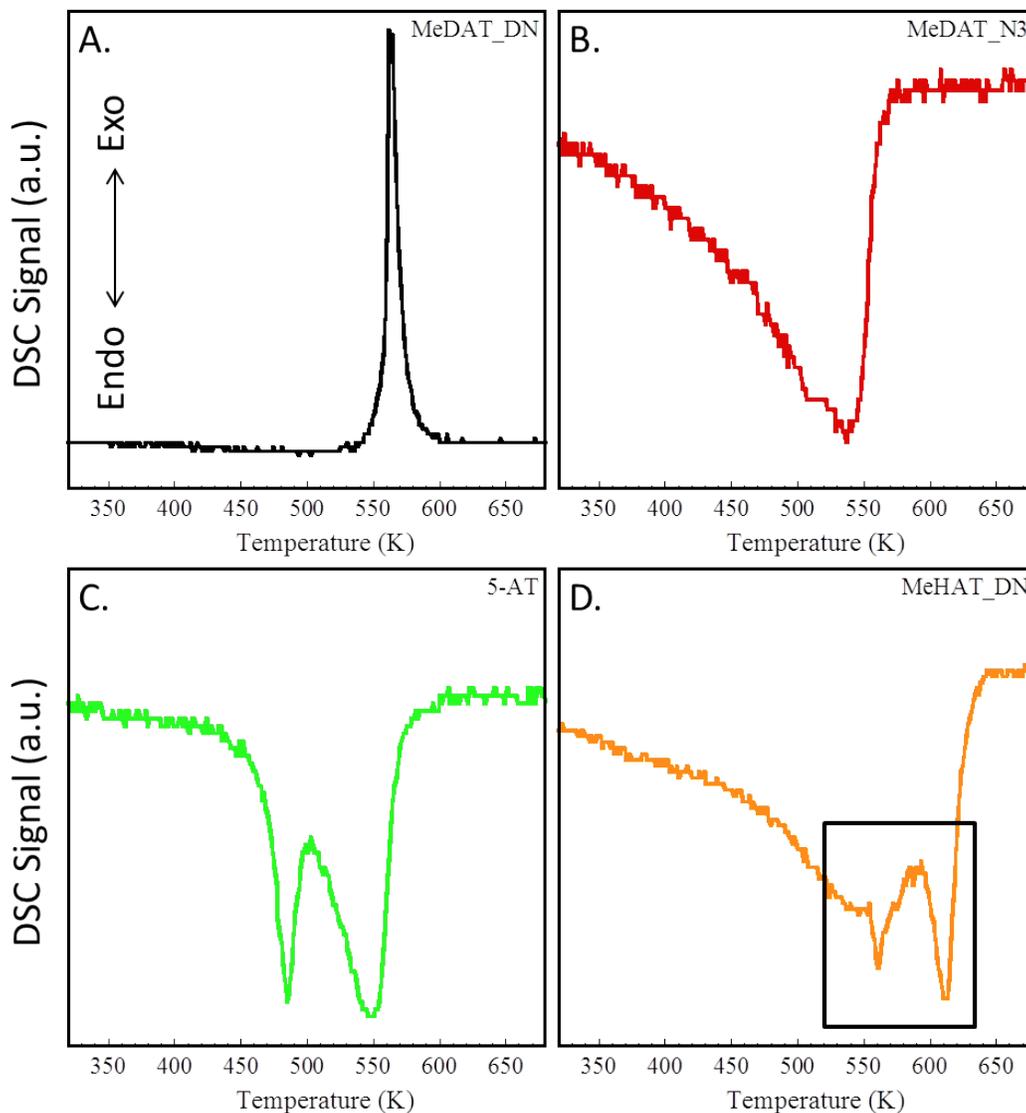


Figure 5: μ -DSC traces with a 6500 K/s sec heating rate for A) Me-DAT_DN, B) Me-DAT_N3, C) 5-AT, D) Me-HAT_DN.

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