



## Rapid-heating of energetic materials using a micro-differential scanning calorimeter

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### ABSTRACT

A micro-differential scanning calorimeter ( $\mu$ -DSC) was employed to study the thermal decomposition of organic energetic materials at high heating rates. Heating rates from 1900 to 65,000 K/s were explored, which are many orders of magnitude higher than traditional DSC, but much closer to the conditions these materials would experience in their application. Temperature calibration was done by heating Sn, KNO<sub>3</sub>, and KClO<sub>4</sub> at the desired heating rates to determine the temperature profile at each rate. The samples studied were 5-amino-1H-tetrazole, 5-amino-1-methyl-1H-tetrazolium dinitramide, 1,5-diamino-4-methyl-1H-tetrazolium dinitramide, and 1,5-diamino-4-methyl-1H-tetrazolium azide, which comprise a new class of high-nitrogen containing energetic materials. Activation energies determined using the Kissinger method, are much lower than those reported for the same materials under low heating rates indicating that other decomposition mechanisms are in play at high heating rates.

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### 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 N<sub>2</sub> 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 is primarily responsible for 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-1H-tetrazolium nitrate [4], 1,5-diamino-4-methyl-1H-tetrazolium dinitramide [4], 1,5-diamino-4-methyl-

1H-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 2–40 K/min, Fischer et al. determined the activation energy of several ionic salts and found them to be in the range of ~101–138 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 Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> films showed the activation energy for film crystallization decreased by more than a factor of four 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 both the heaters and the sample [8–11]. A  $\mu$ -DSC device previously developed at the National Institute of Standards and Technology (NIST) is capable of heating rates up to  $1 \times 10^7$  K/s [11], and was previously used to explore phase changes in Ni/Si thin films [12]. In the present

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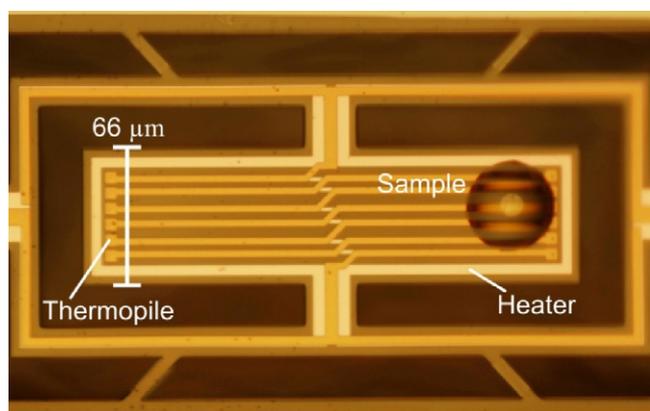


Fig. 1. Image of the  $\mu$ -DSC with a droplet of an organic energetic sample.

study 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  $\mu$ -DSC device [11] ( $66 \times 240 \times 3.3 \mu\text{m}$ ) shown in Fig. 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 are varied by adjusting the frequency of the function generator, and for these experiments the heating rates range from  $\sim 1900$  to  $64,000$  K/s. Samples are placed onto the surface of the  $\mu$ -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, ejecting a droplet from the tip. Drop sizes are determined optically from images such as Fig. 1, and ranged from  $\sim 10 \mu\text{m}$  to  $60 \mu\text{m}$  in diameter. Each sample is initially placed in either ethanol or methanol at a concentration of  $\sim 100$  mg/ml to maintain stability of the material. Samples are then diluted with  $\text{H}_2\text{O}$  to a concentration of  $\sim 10$  mg/ml to prevent drying in the micropipette. The volume of the drop is 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 is taken to be  $30^\circ$  [14] and the curvature of the drop is assumed to be similar to a spherical cap [15]. Assuming the diameter of the drop as viewed in Fig. 1 to be  $60 \mu\text{m}$  the mass of sample is estimated to be 0.1 ng.

All organic energetic materials used in this experiment were provided by T.M. Klapötke of Ludwig-Maximilians University in Munich, Germany. The materials are 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.

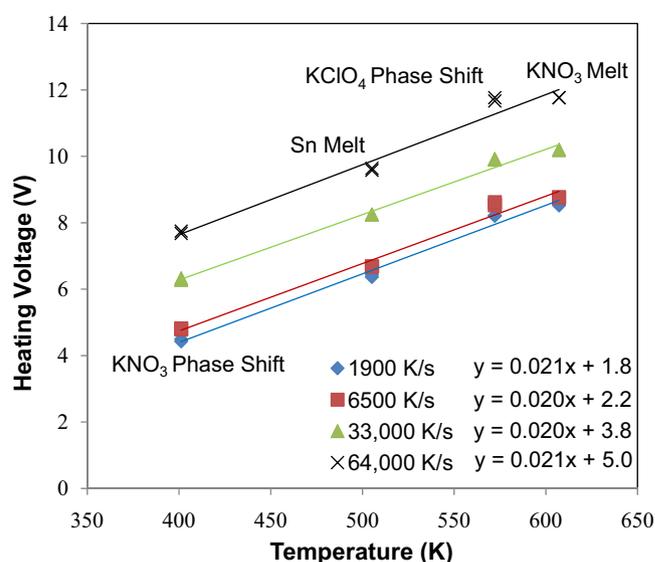


Fig. 2. Voltage to temperature calibration for reference thermal signatures, melting point of tin, 505 K, solid–solid phase transition of  $\text{KClO}_4$ , 572.2 K, solid–solid phase transition of  $\text{KNO}_3$ , 401.2 K, and melting point of  $\text{KNO}_3$ , 607.1 K.

Linear voltage ramps are 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 ( $\text{KClO}_4$ ), and potassium nitrate ( $\text{KNO}_3$ ), which has two calibration points. The known calibration points are the melting point of tin at 505.1 K [19], a solid–solid phase transition for  $\text{KClO}_4$  at 572 K [20], a  $\text{KNO}_3$  solid–solid phase transition at 401 K [20,21], and melting at 607 K [22]. With the known thermal properties of each material, four heating rates are applied,  $\sim 1900$  K/s,  $\sim 6500$  K/s,  $\sim 33,000$  K/s, and  $\sim 64,000$  K/s. For each material the voltage point at the onset of the phase transition was measured and plotted in Fig. 2. A linear function was created to convert voltage to temperature for each heating rate, the results of which are also shown in Fig. 2. To achieve a desired temperature and ramp rate, the voltage and ramp duration are 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 Fig. 3. The error bars represent the standard deviation at each temperature point. We expect that the primary error in this experiment is due to either inconsistencies in drop size and placement, or non-uniformities in the heating surface's temperature profile. Either of these issues would cause slight variations in sample temperature throughout the experiment.

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  $\beta$  is the heating rate,  $T_p$  is the temperature where the calorimetric trace peaks, and  $R$  is the gas constant. Fig. 4 plots the left side of Eq. (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

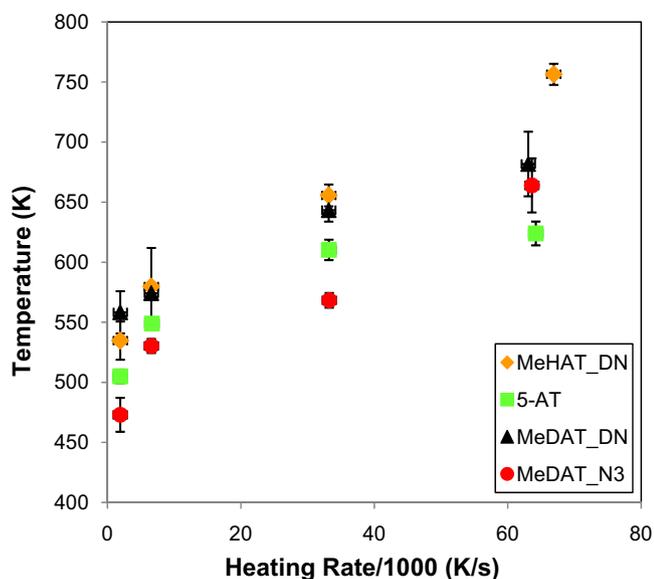


Fig. 3. Decomposition temperature of various materials at four different heating rates.

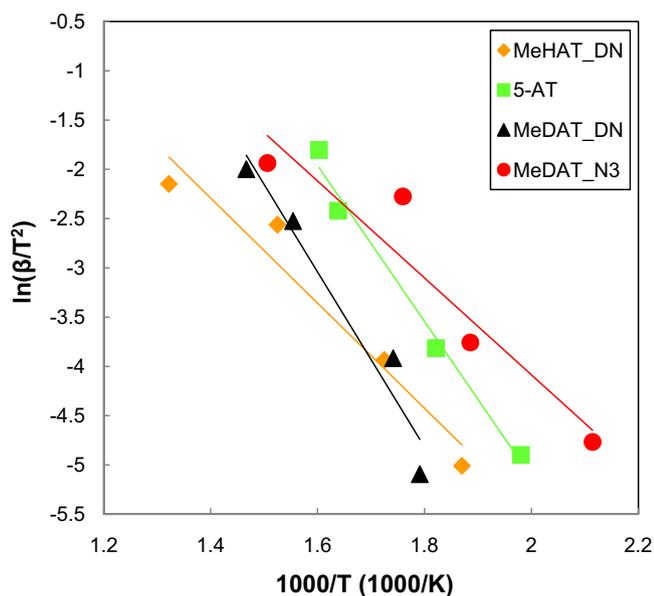


Fig. 4. Kissinger plots for each sample.

trace. Each data point, represents the averaged peak temperature from several runs. The materials in Fig. 4 demonstrate an acceptable degree of linearity, as each sample has a correlation coefficient of 0.95 or greater. Table 1 lists the calculated activation energy and uncertainty for each material. The uncertainty was estimated from a Kissinger plot based on all un-averaged experimental runs, from which the maximum and minimum slope were determined assuming a 95% confidence interval.

Table 1

Activation energies for each material determined from the Kissinger method.

Material	$E_a$ (kJ mol <sup>-1</sup> )
MeDAT_DN	74 ± 14
MeDAT_N3	41 ± 13
5-AT	66 ± 10
MeHAT_DN	44 ± 6.1

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 is 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 Fig. 5a. This is consistent with traditional DSC experiments, which also show a strong exotherm. In this low heating rate study by Fischer, the decomposition peak shifted from 450–488 K for a 2–40 K/min heating rate range [4]. Fig. 3 shows the variance in temperature of the exothermic peak for MeDAT\_DN in the high heating rate  $\mu$ -DSC experiments, which occurs in the range of 558–682 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  $\mu$ -DSC, a shallow broad endotherm is present, and likely represents melting. Through the Kissinger method we calculate the activation energy to be  $\sim 74$  kJ/mol, close to half of the  $\sim 138$  kJ/mol calculated by Fischer et al. through both the Ozawa and Kissinger methods [4]. The uncertainty in activation energy of 14 kJ mol<sup>-1</sup> for MeDAT\_DN is relatively high compared to traditional DSC experiments. Even with this uncertainty, it is still clear that the activation energy is much lower than previous values, indicating that decomposition at high heating rates is clearly different than observed at lower rates.

### 3.2. MeDAT\_N3

MeDAT\_N3 is reported to show an endothermic peak in the range of 458–484 K for various low heating rates, and has a reported melting point of 408 K [4]. In Fig. 5b a large endothermic peak is observed for this material, which is consistent with the low heating rate work [4]. In the  $\mu$ -DSC experiment the peak of the decomposition ranges from 473–664 K, and the activation energy is calculated to be  $\sim 41$  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 for the 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 with a 1  $\mu$ m hole in the top, 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  $\mu$ -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 endothermic event that can be better detected with the sensitivity of the  $\mu$ -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<sub>2</sub>O and ethanol, and are known to have low vapor pressures.

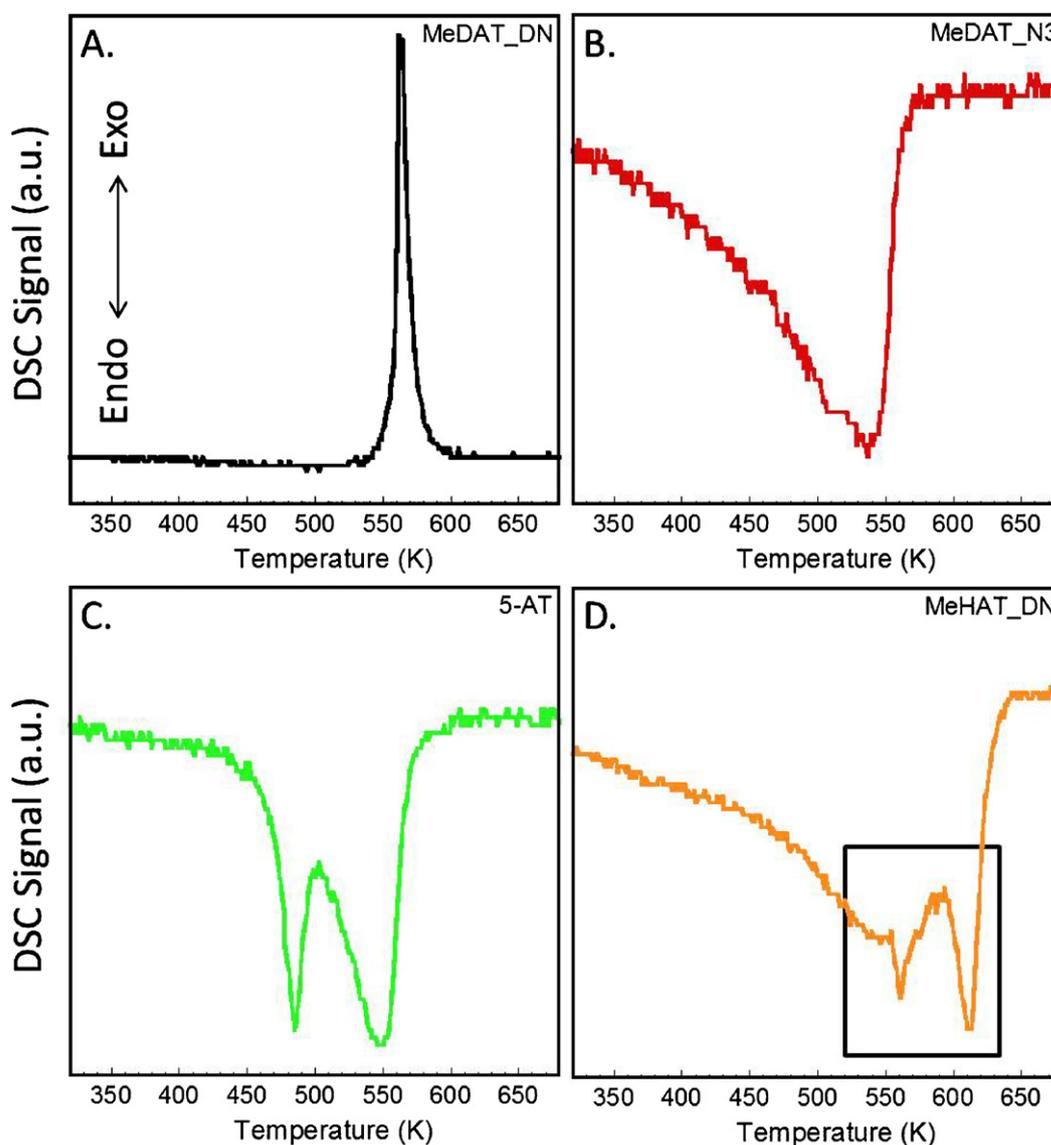


Fig. 5.  $\mu$ -DSC traces with a 6500 K/s heating rate for (A) MeDAT.DN, (B) MeDAT.N3, (C) 5-AT, (D) MeHAT.DN.

### 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 backbone of the cation species in each of the other EMs. This sample at 10 K/min displays a decomposition temperature of 480 K and has a melting point of 478 K [2]. The activation energy was also reported to be 136–153 kJ/mol using several different iso-conversion methods at heating rates of 0.63–40 K/min. Fig. 5c shows a sample  $\mu$ -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 decomposition peak increases with heating rate in the range of 505–624 K. In the Lesnikovich study [2] 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 Fig. 4, the activation energy was calculated to be  $\sim$ 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  $\mu$ -DSC studies the thermal trace of MeHAT.DN in Fig. 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 Fig. 5b. Secondly, we observed a sharp endotherm, shown in the boxed region of Fig. 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 535–757 K and the activation energy for MeHAT.DN is  $\sim$ 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. Conclusion

Decomposition of energetic materials are nominally studied using traditional DSC tools which employ heating rates many orders of magnitude lower than that experienced in a real world application. In this study we employ a  $\mu$ -DSC to study the thermal decomposition of organic energetic materials at high heating rates. Four high nitrogen-containing energetic materials were chosen for the study, for which we found a consistently, and significantly lower activation energy than that found at low heating rates. These significantly lower activation energies imply that other decomposition mechanisms are in play at high heating rates.

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