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STUDY OF THERMAL SENSITIVITY AND THERMAL EXPLOSION VIOLENCE OF ENERGETIC MATERIALS IN THE ODTX SYSTEM

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Study of Thermal Sensitivity and Thermal Explosion Violence of Energetic Materials in the ODTX System

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Abstract. The One Dimensional Time to Explosion (ODTX) system at the Lawrence Livermore National Laboratory has been used since 1970s to measure times to explosion, threshold thermal explosion temperature, and determine kinetic parameters of energetic materials. The ODTX testing can also provide useful data for assessing the thermal explosion violence of energetic materials. It is a useful tool for the characterization of newly developed energetic formulations. Recent ODTX experimental data as well as data modeling for ANPZ and DMDNP will be reported in this paper. More diagnostics are being added to the system to enhance its capability

Introduction

Some energetic materials (e.g., hydrogen peroxide/fuel mixtures[1]) may explode (cook-off) at fairly low temperatures and the violence from the thermal explosion may cause a significant damage. Thus it is important to understand the response of energetic materials to thermal insults for safe handling and storage of energetic materials. There has been an extensive study on the thermal decomposition and thermal explosion violence of energetic materials at elevated temperatures in different confinements and sample geometries (one-dimensional and two-dimensional) [2,3,4]. Thermal explosion studies on various energetic materials in two-dimensional geometry such as the Scaled-Thermal-Explosion-Experiment (STEX) system[5] and the Sandia-Instrumented-Thermal-Ignition (SITI) system were previously reported[6]. The ODTX system at the Lawrence Livermore National Laboratory (LLNL) has been used for decades for cook-off study[7-11]. It is attractive due to the minimal sample requirement, up to 2 grams for each ODTX shot. The ODTX testing generates three technical data: (1) lowest temperature at which thermal explosion would occur (threshold temperature, T_{li}); (2) times to thermal explosion at temperatures above T_{li} for the calculation of activation energy and frequency factor; and (3) thermal explosion violence. It is a useful tool that is being used routinely at LLNL for the characterization of new energetic materials at LLNL.

Experiments and Results

Energetic materials in any sample configurations (except gaseous samples) can be tested in the ODTX system. An aluminum shell is used to hold powder samples, pasty samples, or liquid samples. Pressed and cast samples are delivered to the cavity of aluminum anvils directly without the use of the aluminum shell. The testing involves heating a 1.27-cm diameter spherical sample in a spherical cavity between two aluminum anvils. The sample is remotely delivered to the anvil cavity via the sample delivery system when the anvils reach a predetermined temperature. A microphone sensor measures a sound signal, which indicates the time at which a thermal explosion occurs. The detail description of the LLNL ODTX system can be found elsewhere [1].

Small-scale Safety Test Results on ANPZ and DMDNP, and LLM-105

2,6-diamino-3,5-dintropyrazine (ANPZ) and 2,6-dimethoxy-3,5-dinitropyrazine (DMDNP) are energetic materials that are intermediate products in the synthesis of LLM-105 (2,6-diamino-3,5-dintropyrazine-1-oxide). LLM-105 is a potential insensitive high explosive under development at LLNL. LLM-105 is attractive for its high density and good performance[12]. Both ANPZ and DMDNP are very insensitive to impact and have DSC peak exotherms at 356 °C and 277 °C, respectively. DMDNP melts at 164 °C Table 1 lists the small scale safety test data for comparison.

Table 1. Small scale safety test results for DMDNP, ANPZ and LLM-105.

Tests	**LLM-105**	**ANPZ**	**DMDNP**
Impact sensitivity (drop hammer), cm	91	> 177	> 177
Friction sensitivity, kg	0/10 @ 36.0 kg	0/10 @ 36.0 kg	0/10 @ 36.0 kg
Spark sensitivity	0/10 @ 1.0 J @ 510 Ohms	0/10 @ 1.0 J @ 510 Ohms	0/10 @ 1.0 J @ 510 Ohms
Chemical Reactivity (CRT) at 120 °C	0.2 cc/g	0.03 cc/g	0.05 cc/g
DSC	Peak temperature at 361 °C	Peak temperature at 356 °C	Peak temperature at 277 C, melted at 164 °C
Density, g/cc	1.918	1.840	1.640

Although LLM-105 is more impact-sensitivity than ANPZ and DMDNP, it is more desirable for its higher density.

ODTX Times to Explosion Data for ANPZ and DMDNP

Both ANPZ and DMDNP were pressed into 0.5 inch spherical parts, as shown in Fig. 1 and Fig. 2. Pressibility of the materials was good without the use of binder, though pressed density was somewhat limited to around 93% TMD. These parts were tested in the ODTX system over a range of temperature. Totally over 10 ODTX shots were performed on each materials and the times to thermal explosion data are shown in Table 2 and Table 3, respectively. The test data are plotted in Figure 3. The figure also shows ODTX data for PETN, RDX, HMX, and TATB for comparison. Also shown is RX-55-AA (from ODTX tests done in 1996), which consists of LLM-105 and Viton. The ODTX test results indicated that the thermal sensitivity of ANPZ was between those of TATB and HMX and was somewhat less sensitive than RX-55-AA. DMDNP was more sensitive than ANPZ and similar to HMX. Reproducibility of tests was excellent. Testing was repeated at a few temperatures for both materials and the results were fairly close.

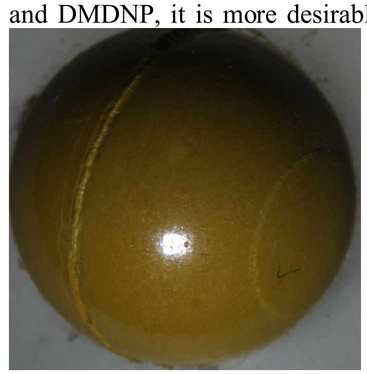

Fig. 1. ANPZ pressed sphere, 0.5” in diameter, 92.5% TMD (1.7 g/cc).

Fig. 2. DMDNP pressed sphere, 0.5” in diameter, 93.8% TMD (1.54 g/cc).

Table 2. Times to thermal explosion data for ANPZ

Test #	Temp., °C	Time to Explosion, second	Note
1	333.8	61	
2	314.1	147	
3	314.1	157	Repeated
4	298.3	170	
5	282.4	235	
6	282.4	247	
7	267.4	503	
8	253.2	1294	
9	253.2	1284	Repeated
10	239.7	4120	
11	226.9	12387	
12	214.7	34425	
13	192.0	167826 (46.6 hours)	No thermal explosion (NO-GO)

Table 3. Times to thermal explosion data for DMDNP

Test #	Temp., °C	Time to Explosion, second	Note
1	298.3	11	
2	282.4	18	
3	282.4	21	Repeated
4	267.4	40	
5	253.2	55	
6	239.7	191	
7	226.9	386	
8	226.9	412	Repeated
9	214.7	1415	
10	203.0	5098	
11	192.0	11084	
12	181.4	96072 (26.7 hours)	No thermal explosion (NO-GO)

Table 4 shows the lowest temperatures at which thermal explosion (threshold temperature, T_{li}) would occur. ODTX testing on ANPZ at 192 °C for 46.6 hours showed no thermal explosion but thermal explosion occurred after 9.56 hours (34,425 seconds) at 214.7 °C. Thus the threshold temperature for ANPZ is less than 214.7 °C and higher than 192.0 °C. For DMDNP at 181.4 °C, the threshold temperature is less than 192.0 °C and higher than 181.4 °C.

Table 4. Threshold temperature for thermal explosion (T_{li})

Materials	T_{li}, °C
PETN	130
RDX	175
HMX	180
DMDNP	Between 181 and 192
RX-55-AA	190
TNT	200
ANPZ	Between 192 and 215
TATB	230

Thermal Explosion Violence

After thermal explosion, each aluminum anvil is inspected to determine the cavity size expansion. Fig 3 shows the anvils before and after the thermal explosion. The anvils indicated some melting from the extremely hot gas generated by the explosion. The blast energy (energy of explosion) from the thermal explosion can be estimated from the crater size in the aluminum anvils[7,11]. A visual inspection and estimation shows the cavity volume increases for both materials tested were all significantly less than that for HMX-based formulations.

Fig. 3. pristine anvil (top left); spent anvils for ANPZ (top right) DMDNP (bottom right) and PBX-9501 (bottom left).

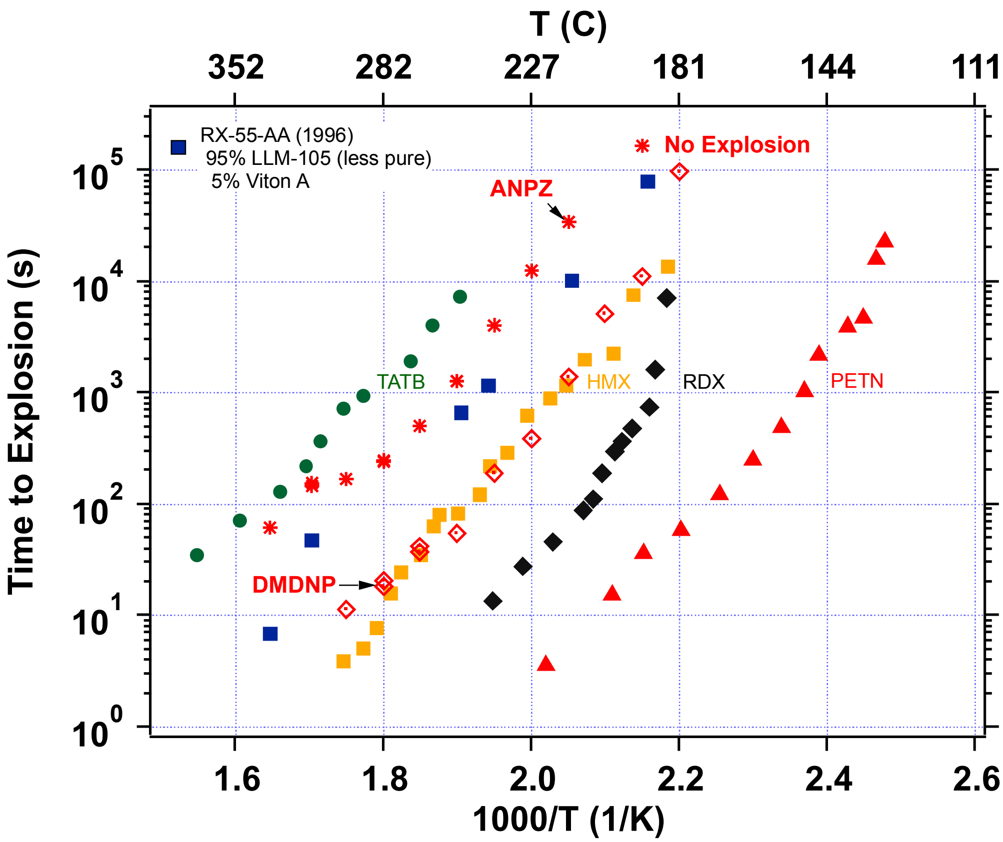

Fig. 4. ODTX results for ANPZ, AMDNP, RX-55-Aa and several commonly-used high explosives: PETN, RDX, HMX, and TATB.

ODTX Modeling for ANPZ and DMDNP

The times to explosion data for both materials can be modeled to obtain their thermal decomposition kinetic parameters, as represented by a single-step Prout-Tompkins (Arrhenius) equation[13, 14].

$$\frac{dx}{dt} = -A\exp\left(-\frac{E}{RT}\right)x^n\left(1-qx\right)^m, \quad (1)$$

where x = mass fraction of reactant remaining, dimensionless; A = frequency factor, $second^{-1}$; E = the activation energy, J/mole; R = universal gas constant, 8.314 J/(K.mol); T = temperature, K; n, m, q = Prout-Tompkins model kinetics parameters, dimensionless.

It is also convenient to define

$P=-\log_{10}(1-q)$ (2)

For ODTX data modeling, E/R, A, and p were adjusted with m=n=1 to fit ODTX experimental data. A is the frequency factor or characteristic reaction rate, and the quantity E/R specifies the temperature sensitivity. The parameter p generates a characteristic time delay for the reaction of the scale p/A for m=n=1. The parameter m has a strong effect on reaction progress in the early stages of the reaction when x~1, while n is important for progress during the later stages of the reaction when x~0. The measured explosion times in this study provide data for the end time of thermal decomposition, but no information related to the earlier progress of the reaction. Consequently, we set m=n=1. Finally it is noted that most ODTX reactions do not progress very far with (1-x) less than 10% before thermal runaway, ignition, and explosion. The kinetic parameters for thermal decomposition are listed in Table 4. (1)

Table 4. Kinetic parameters for thermal decomposition

Parameter	ANPZ	DMDNP
ln(A), s^{-1}	21.72	32.61
E/R, K^{-1}	14,548	18,815
p	3.17	3.02
m	1.0	1.0
n	1.0	1.0

The model and measured explosion times for ANPZ and DMDNP are plotted versus 1/T in Fig. 5 and Fig. 6. Although the model does not capture all of the features of the measurements, it does provide a good overall representation of the data.

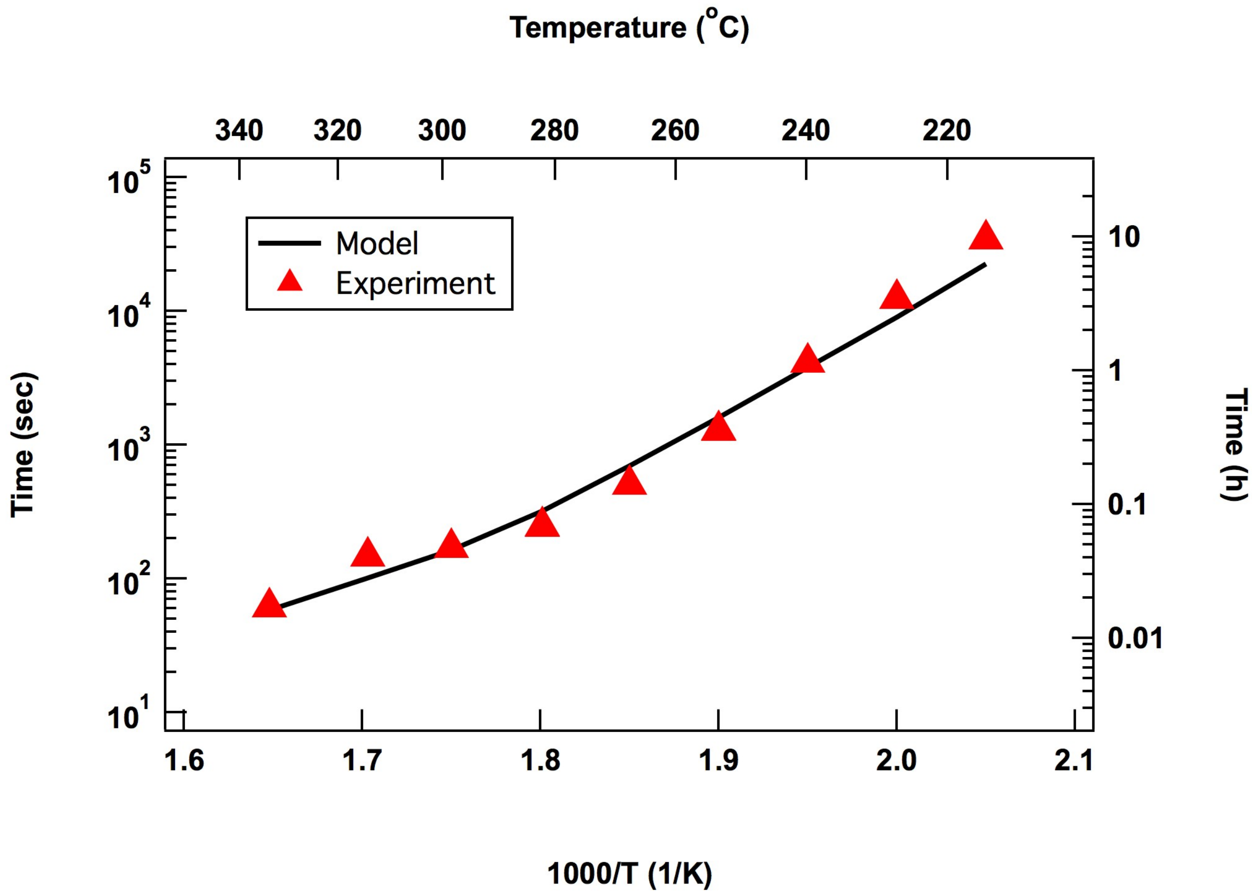

Fig. 5. Comparison of model and experimental data for ANPZ.

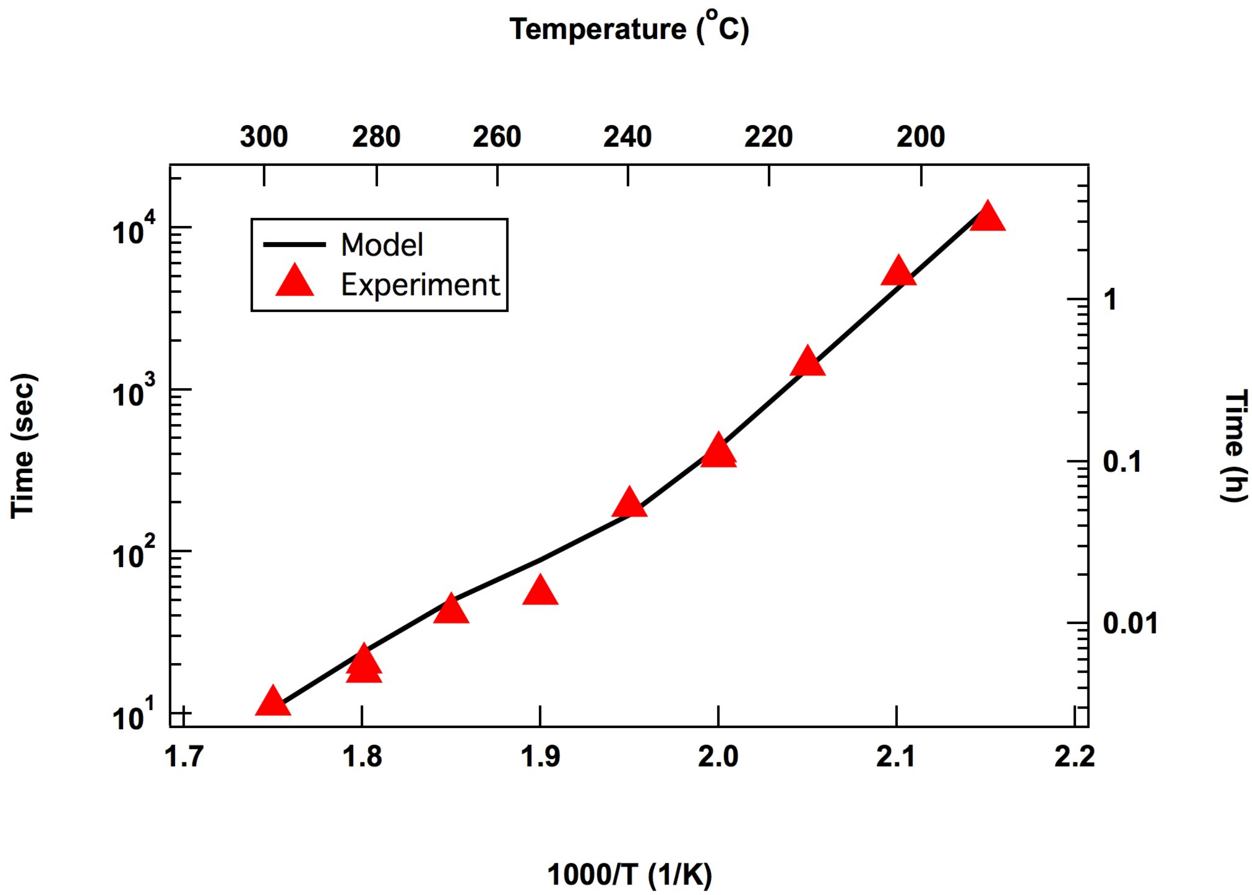

Fig. 6. Comparison of model and measured ODTX explosion times for DMDNP.

Conclusions

The ODTX system is being used for the IHE qualification test as well as for the measurement of thermal sensitivity, thermal decomposition kinetic parameters, and thermal explosion violence. Samples of all configurations (solids, powders, pastes, and liquids) can be tested in the system. Results of ODTX testing on ANPZ showed that its thermal sensitivity is between those of TATB and HMX with low thermal explosion violence. The threshold temperature for thermal explosion for ANPZ is also higher than that of HMX but lower than that of TATB. Test results of DMDNP showed it also had low thermal explosion violence with thermal sensitivity similar to HMX. The experimental data for both ANPZ and DMDNP have been parameterized into a model that is available in the LLNL's ALE3D code for other cook-off systems of interest.

Future Work

We are adding more diagnostics to the ODTX system to improve its capability. Pressure transducer can monitor the gas pressure in-situ and have been implemented as part of the system. The pressure data is important to understand the thermal decomposition kinetics of energetic materials and will be used to validate cook-off models. In the future, gas analytical instruments could be added to the system as well to measure the gas composition when material is under thermal insults.

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