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One-Dimensional Time to Explosion (Thermal Sensitivity) of DMDNP

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Abstract. Incidents caused by fire and combat operations can heat energetic materials that may lead to thermal explosion and result in structural damage and casualty. Some explosives may thermally explode at fairly low temperatures (< 100 C) and the violence from thermal explosion may cause a significant damage. Thus it is important to understand the response of energetic materials to thermal insults. The One Dimensional Time to Explosion (ODTX) system at the Lawrence Livermore National Laboratory has been used for decades to measure times to explosion, threshold thermal explosion temperature, and determine kinetic parameters of energetic materials. Samples of different configurations (pressed part, powder, paste, and liquid) can be tested in the system. The ODTX testing can also provide useful data for assessing the thermal explosion violence of energetic materials. This report summarizes the recent ODTX experimental data and modeling results for 2,6-dimethoxy-3,5-dinitropyrazine (DMDNP).

1. Introduction

Accidents involving with thermal explosion (or cook-off) of energetic materials are costly. Over the last few decades, there has been considerable research effort on the thermal decomposition and thermal explosion violence of energetic materials at elevated temperatures in different sample geometries and confinement [1-3]. Thermal explosion studies on various energetic materials in two-dimensional geometry such as the Scaled-Thermal-Explosion-Experiment (STEX) system [4] and the Sandia-Instrumented-Thermal-Ignition (SITI) system have been reported [5]. The One Dimensional Time to Explosion (ODTX) system at the Lawrence Livermore National Laboratory (LLNL) has been used since 1970s for cook-off study [6-10]. It is attractive because of the one-dimensional geometry, providing a minimal sample requirement (up to 2 grams for each test) and low cost. 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.

2. A brief description of ODTX capability at LLNL

Understanding the response of energetic materials to thermal incidents is very important for the handling, storage and transportation of energetic materials. The uniqueness of the ODTX system at LLNL is because of its capability to generate three important technical data, which are described below.

(1) lowest temperature at which thermal ignition would occur (T_{li}),
(2) times to thermal explosion at temperatures above T_{li} for the calculation of activation energy and frequency factor for thermal decomposition kinetics,
(3) Thermal ignition/explosion violence

(1) $\boldsymbol{T_{li}}$

Knowing the lowest thermal ignition temperature (T_{li}) for each energetic material is very important for safe storage and transportation to avoid incidental detonation. Two possible scenarios for causing incidental thermal explosions are described below:

1. Energetic materials may be kept and stored in closed containers that are exposed to hot climates. During the summer in some desert areas, outdoor temperature may exceed 120°F while the surface temperature of metallic storage containers exposed to the sun may exceed 170°F (77°C). Given enough time, some energetic materials may ignite and explode.
2. If containers storing energetic materials are kept inside a parked van or truck with windows closed for an extended period of time, the air inside the van may exceed 170°F in the summer. Given enough time, some energetic materials in the containers may ignite and explode.

(2) ***Time to Explosion Data, Activation Energy, and Frequency Factor***
Times to thermal explosion at temperatures above T_{li} for the calculation of activation energy and frequency factor as well as the decomposition kinetics parameters represented by a single-step Prout-Tompkins (Arrhenius) model (shown in the modeling section).

(3) ***Thermal Explosion Violence***
Violence from thermal explosion is an important parameter for cook off study. After the ODTX testing, each anvil was scanned with a surface profilometer to determine the cavity volume increase. Figure 1 shows anvils before and after the thermal explosion from the ODTX testing. The violent thermal explosion discolored the anvils and created craters in the anvils.

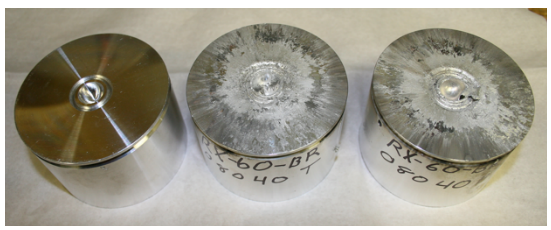

Figure 1. Anvils before and after thermal explosion of a liquid explosive; left was the pristine anvil; also shown are top anvil (middle) and bottom anvil (right) after the thermal explosion.

3. Comparison of ODTX with DSC

Both ODTX and DSC can generate thermal kinetic data for homogeneous explosive samples. For heterogeneous sample mixtures, ODTX is preferred because its sample size of 2 grams is much larger than the DSC sample size of 0.3 mg. Below are several things that ODTX can generate and DSC cannot.

1. The minimum temperature for thermal explosion to occur

   Knowing the minimum temperature for thermal explosion to occur is very important for safe storage and handling of energetic materials. The ability of testing explosive in the ODTX system at lower temperatures until no thermal explosion occurs allows for the determination of fairly precise threshold temperature for thermal explosion to occur. Both DSC and Cheetah do not provide the information.

2. Thermal explosion violence
   Violence from thermal explosion is one of the important parameters for explosive safety. Careful monitoring of anvil cavity volume increase before and after thermal explosion allows for the determination of thermal explosion violence. DSC and Cheetah cannot predict nor measure the thermal explosion violence.

3. Samples of different density and configuration
   Samples of any density and any configurations (solid pressed parts, powders, pastes, and liquids) can be tested in the ODTX system. Sample size is much larger than that for DSC (2.0 g for ODTX and ~ 0.3 mg for DSC). Since DSC sample size is less than 1.0 mg, it is difficult to get a good representative sample for a heterogeneous mixture. Thus obtaining thermal decomposition kinetic on hetergenerous mixtures from DSC data may not be accurate.

4. System Description and Experiments

The ODTX system, as shown in figure 2, is operated remotely in a test cell. 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 [11].

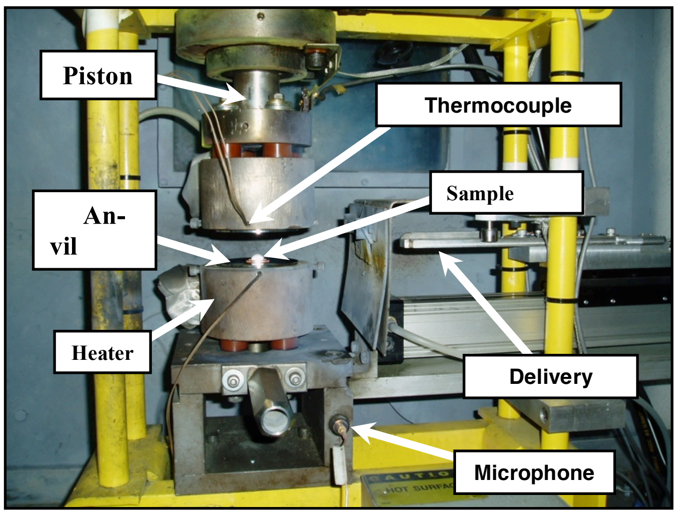

Figure 2. LLNL ODTX system.

Samples of various configurations (pressed parts, cast parts, powders, pastes, and liquids) can be tested in the ODTX system. Pressed and cast samples are loaded into the cavity of aluminum anvils directly without secondary containment. An aluminum shell is used as a secondary containment to hold powder samples, pasty samples, or liquid samples before loading to the system. ODTX tests are typically run 10 to 20 times at various temperatures to obtain time to thermal explosion charts. The tests require a total of 30 grams of material.

5. ODTX test results on DMDNP

5.1 Small-scale safety tests for DMDNP

DMDNP is an energetic material which is a precursor to ANPZ (2,6-diamino-3,5-dintropyrazine). Small scale safety test (SSST) results showed both DMDNP and ANPZ are less sensitive to impact and thermal insults than LLM-105, see table 1 for comparison. These test results are recently performed at LLNL. Although LLM-105 is more sensitive but it is desirable for its higher density.

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

- Recrystallized DAPO LLM-105 with 99% purity, tests done in May 2013
- Recrystallized ANPZ, tests done in November 2013

5.2 ODTX Times to Explosion Data for DMDNP

DMDNP powder (light gray color) was pressed into 0.5 inch spherical parts, as shown in Figure 3, with a bulk density of 1.54 g/cc (93.8% TMD). These parts were tested in the ODTX system over a range of temperature. Totally 12 ODTX shots were performed and the times to thermal explosion are shown in Table 2. The test data are plotted in Figure 4. The figure also shows ODTX data for PETN, RDX, HMX, and TATB. Also shown are ANPZ (recently performed) and RX-55-AA (95.0% LLM-105, 5% Viton, done in 1996 with less pure LLM-105). The ODTX test results indicated that DMDNP is more sensitive than RX-55-AA and ANPZ and is similar to HMX.

Reproducibility was excellent. Testing was repeated at two temperatures (282.4 C and 226.4 C) and results were close.

Table 3 shows the lowest temperatures at which thermal explosion (threshold temperature, T_{li}) would occur. ODTX testing on DMDNP at 181.4 C for 26.7 hours showed no thermal explosion but thermal explosion occurred after 3.08 hours (11,084 seconds) at 192.0 C. Thus the threshold temperature for DMDNP is less than 192.0 C and higher than 181.4 C.

Figure 3. DMDNP pressed sphere, 0.5” in diameter, 93.8% TMD (1.54 g/cc).

Table 2. ODTX Data For DMDNP
E = 156 KJ/mole, A = 1.5 x 10^{14} $second^{-1}$
(From the modeling results in Table 5)

Test number	Temperature, °C	Time to explosion, sec	Note
1	298.3	11.3	
2	282.4	18.1	
3	282.4	20.5	Reproducibility study
4	267.4	40	Two bursts
5	253.2	54.7	
6	239.7	190.9	
7	226.9	385.8	
8	226.9	411.6	Reproducibility study
9	214.7	1,414.9	
10	203.0	5,098.4	
11	192.0	11,083.8	
12	181.4	96,072 (26.7 hours)	No thermal explosion (NO-GO)

Table 3. Threshold temperature for thermal explosion (T_{li}) for DMDNP

Materials	T_{li}, °C
PETN	130.0
RDX	180.0
HMX	180.0
DMDNP	Between 181. C and 192.0 C
RX-55-AA	190
TNT	200
ANPZ	Between 192 and 214.7 C
TATB	230.0

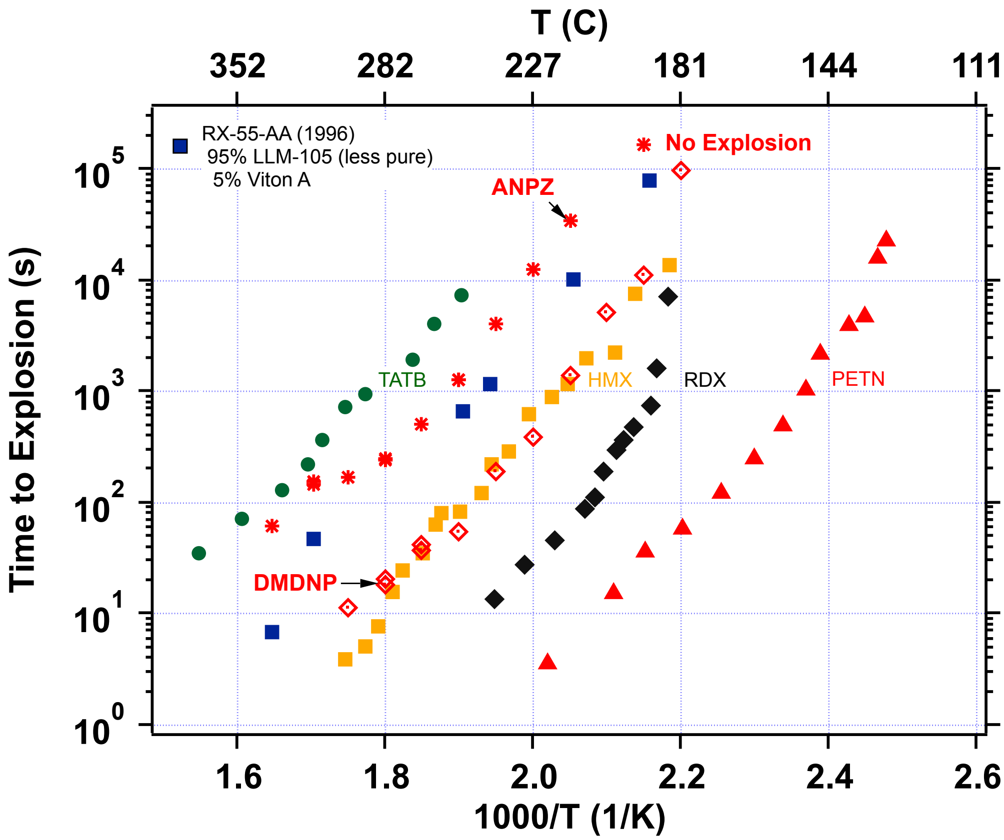

Figure 4. ODTX results of DMDNP, ANPZ, RX-55-AA, and several commonly-used high explosives HMX, PETN, RDX, and TATB.

5.3. Thermal explosion violence of DMDNP

Figure 5 shows the anvils before and after the thermal explosion of DMDNP. 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 [3, 11]. Due to the funding constraint, no cavity volume increase was measured with the surface profilemeter to quantitatively determine the thermal explosion violence. But a visual inspection and estimation shows the cavity volume increases for DMDNP tested were all significantly less than that for HMX-based formulations.

Figure 5. Anvils before and after thermal explosion of DMDNP at 253.2 C; left was the pristine anvil; also shown are top anvil (middle) and bottom anvil (right) after the thermal explosion.

5. ODTX Modeling for DMDNP

5.1. Thermal-kinetic model

The kinetics model parameters are determined for DMDNP by nonlinear regression using a transient one-dimensional model of chemical reaction and thermal conduction with heat generated by decomposition. It is assumed that heat flows, the energetic material decomposes, but material does not flow. This is a good assumption prior to ignition for explosives with high melting points. However, DMDNP has a melting point of ~164 °C and is fully liquid and flowing in the longer experiments. As discussed more below, this thermal-kinetics model is much more approximate for DMDNP, and the resulting kinetics model will need to be used with a thermal fluids model for all but the fastest heating rates in larger scale systems.

The decomposition kinetics of DMDNP are represented by a single-step Prout-Tompkins (Arrhenius) model [12].

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

in which

x = mass fraction of reactant
A = frequency factor
E = the activation energy
R = universal gas constant
T = temperature
n, m, q = Prout-Tompkins model kinetics parameters

It is also convenient to define

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

For DMDNP, the parameters E/R, A, and p were adjusted with m=n=1 to fit ODTX measurements as described below in section 5.3. 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 the bulk 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.

5.2. Thermal transport properties

The thermal transport properties are listed in Table 4. In this simple model, the density is assumed to be uniform and constant at the measured room temperature value of 1540 kg/m^3, which is 93.9% of maximum density. For the DMDNP reactant, we use a single heat capacity and thermal conductivity representative for a similar material RX-55-AE-5 (97.5 w% LLM-105, 2.5 w% Viton A) near 100 °C [12].

For the gas product we use the reactant value for the heat capacity and a smaller value of the thermal conductivity. In this 1D model the mixture properties are linearly weighted by the mass fraction. However, the influence of the product properties is minimal since the conversion of reactant to product is small at the time of ignition, as mentioned above.

Table 4. Material properties of DMDNP species

	DMDNP reactant	DMDNP product
Material density (kg/m^3)	1540	1540
Heat capacity (J/(kg-K))	1200	1200
Thermal conductivity (W/(m-K))	0.5	0.01
Energy of reaction (J/kg)	0	$4.18x10^6$

5.3 Kinetic parameter from non-liner regression

The parameters A, E/R, and p of Eqs. (1) and (2) with m=n=1 were adjusted using the Microsoft Solver nonlinear regression routine to provide a representation of the measured explosion times. A user-defined VBA function was used to calculate the model explosion times and compare them to the measured values. The 1D transient heat conduction equation was solved using a second-order finite difference method with a uniform mesh, and the time integration was performed with the second-order Trapezoid Rule incorporating variable step-size to control the local error. A temperature of 773 K was specified as the ignition temperature, and a second order interpolation method was used to calculate the explosion time from the results of time steps before and after the ignition temperature. Model explosion times were compared with ALE3D results to verify the calculation method.

In order to make the parameter searches as orthogonal as possible, Eq. (1) was rewritten as

$$\frac{dx}{dt} = -A_0 \exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] x^n \left(1-qx\right)^m \qquad (3)$$

in which T_0 is a temperature in the middle of the measurement range. The addition of T_0 provides an approach analogous to using the orthogonal Legendre polynomials in curve fitting. The search was performed on the variables E/R, $ln(A_0)$, and the quantity $[A_0 \cdot t_{expl,0} - p \cdot ln(10)]$. Here $t_{expl,0}$ is the measured explosion time at T_0. The quantity $[A_0 \cdot t_{expl,0} - p \cdot ln(10)]$ is characteristic of the extent of reaction at ignition, and was used in place of p in an attempt to decouple its variation from changes in E/R and A_0.

For DMDNP, the three-parameter search was performed with 100 zones for the small explosion times and 10 zones for the long explosion times, and could be completed in an hour of wall clock time. Note that finer meshes are needed for small explosion times since all of the activity is confined to thin layers near the outside boundary. Meshes with 2X the above number of zones were used in the model-measurement comparison below.

5.4. Comparison of thermal explosion times for DMDNP

The nonlinear regression procedure was performed for the 1D thermo-chemical model to yield the kinetics parameters given in Table 5. The model and measured explosion times for DMDNP are plotted versus 1/T in Figure 6. Although the model does not capture all of the features of the measurements, it does provide a good overall representation of the data. It is noted that at the low temperature of 181 °C, the model predicts that no ignition takes place which is consistent with the absence of an explosion in the experiment at 26.7 h. Consequently, the model critical temperature is between 181 °C and the lowest measured temperature of ignition, 191 °C. In this temperature range the model explosion times are very sensitive to both physical and numerical parameters, and the model should be used with caution in this area.

The effects of liquid flow need to be considered both in the evaluation of the decomposition model and the application to cook-off scenarios of interest. All of the ODTX temperatures are above the melting point of ~164 °C, indicating flowing liquid in all cases. The characteristic thermal diffusion time of $t_\alpha = R^2 \rho C_p / k = 149$ sec = $(0.00635\ m)^2 (1540\ kg/m^3)(1200\ J/kg\text{-}°C)/(0.5\ W/m\text{-}°C)$, suggests that a significant fraction of the explosive is melted in all but the highest temperature measurements. Thus, the melting and flow of the physical system will give larger thermal transport than assumed in the no-flow model of this study. Since the molecular weight of DMDNP is relatively small at 230, the viscosity is expected to be small, which would contribute to flow. The thermal buoyancies of liquid explosives such as TNT are high and the thermal diffusivities are low, which would generally contribute to thermal convection. However, the small size of the ODTX cavity tends to emphasize the effects of conduction, mitigating the effect of flow on the time to explosion. The measurement of thermal and flow properties combined with thermal-fluids calculations is needed to quantify these effects on the ODTX measurements.

Although flow may alter the ODTX thermal decomposition, its influence will likely increase dramatically in large-scale cook-off systems. For these larger systems, a thermal-fluids model of the type being used with ALE3D is needed to provide better predictions of the effects of flow and melting on explosion times.

Table 5. Chemical kinetics parameters in Eq. (1) for thermal decomposition of DMDNP.

Parameter	Value
ln(A) (s^{-1})	32.61
E/R (1/K)	18,815
p	3.02
m	1.0
n	1.0

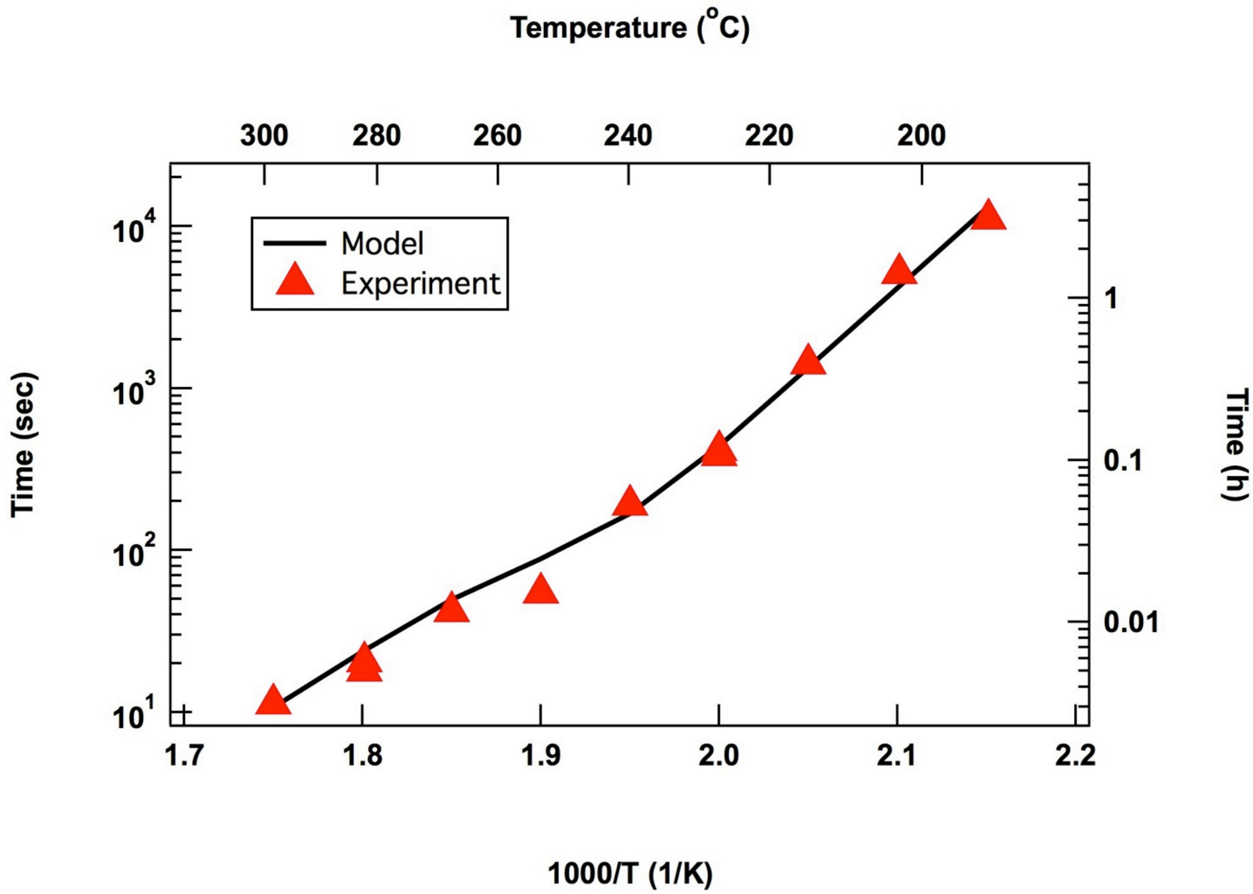

Figure 1. Comparison of model and measured ODTX explosion times for DMDNP.

6. Summary and conclusions

The ODTX system is being used for the IHE qualification test as well as for the measurements of thermal sensitivity, thermal decomposition kinetic parameters, and thermal explosion violence. Samples in various configurations can be tested. Results of the ODTX testing on DMDNP showed that its thermal sensitivity is lower than RX-55-AA and ANPZ and is similar to that of HMX with low thermal explosion violence. The threshold temperature of DMDNP is also close that of HMX but lower than that of ANPZ. The experimental data has been parameterized into a model available in the ALE3D code for other cook-off systems of interest.

Acknowledgments

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