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Recent Advances on Thermal Safety Characterization of Energetic Materials

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Abstract. Understanding the response of energetic material to thermal insults is very important for the storage, transportation, and handling of energetic materials. One dimensional time to explosion (ODTX) is one approach to characterize thermal behavior. Time to explosion and explosion violence have been measured on many materials and the data have been used for the construction of cook-off models. Recent upgrades to the ODTX system allow monitoring of gas pressure (P-ODTX) during thermal experiments, which is important for the model validation. This paper addresses recent ODTX data on time to explosion and thermal explosion violence; P-ODTX data on cook-off temperature and pressure behavior during thermal explosion; C-ODTX data on development of gas evolution monitoring during heating of explosives under confinement.

1. INTRODUCTION

The ODTX (One Dimensional Time to Explosion) technique was developed to enhance the understanding of thermal sensitivity of energetic materials[1]. The technique has been used to measure such thermal properties as time to explosion and lowest temperature for thermal explosion, yielding information such as activation energies and decomposition parameters to fit into kinetic expressions[2]. From the inception around 1970, modifications have been realized to better address mechanisms and models for thermal degradation. Recent modifications include: 1) determination of explosion violence at different heating rates and end temperatures (ODTX)[3,4,5], 2) determination of pressure behavior during decomposition (under confinement) from different cook-off temperatures and partial thermal damage conditions (P-ODTX)[6], and 3) more recently, determination of the chemical identity and concentration of gas species evolving during thermal excursions (C-ODTX). The ODTX systems allow for working with small amounts of materials under confinement.

As examples of the application of ODTX and variants, P-ODTX and C-ODTX, this report summarizes the behavior of LLM-105 (diamino-3,5-dinitropyrazine-1-oxide) a recently synthesized insensitive high explosive[7], to variable cook-off conditions (ODTX), to explosive violence measurements (ODTX), and to pressure monitoring and end temperatures during cook-off (P-ODTX). In addition, this report also summarizes results from testing the initial design for monitoring chemical composition of gas evolution during thermal excursions (C-ODTX).

2. EXPERIMENTAL

System description. The ODTX system has been described in detail elsewhere[4,8]. Briefly, a 1.27-cm diameter spherical sample (pressed parts, powders, pastes and liquids) is placed in an aluminum (Al) cavity. The sample is placed between two Al anvils. The anvils are closed and around the sealed in place with a metal gasket. A microphone sensor measures a sound signal that determines when thermal explosion occurs. Programmed heating is used to produce thermal profiles. The anvils are kept under pressure to keep the pressure on the system. About 10 ODTX tests are performed on a material at different temperatures to obtain times to thermal explosion data. Reproducibility of the testing is within ± 5%. The detail description of the LLNL ODTX system can be found elsewhere [6,7].

The P-ODTX system has also been described elsewhere[6]. The upper anvil, however, has been modified to connect a pressure transducer. To accommodate the rapid pressure change occurring near explosion, the system is also equipped with a rapid monitoring system that records data every μsec. This allows for much higher resolution of pressure change near explosion. The C-ODTX system operated under the same protocols as the ODTX and P-ODTX experiments.

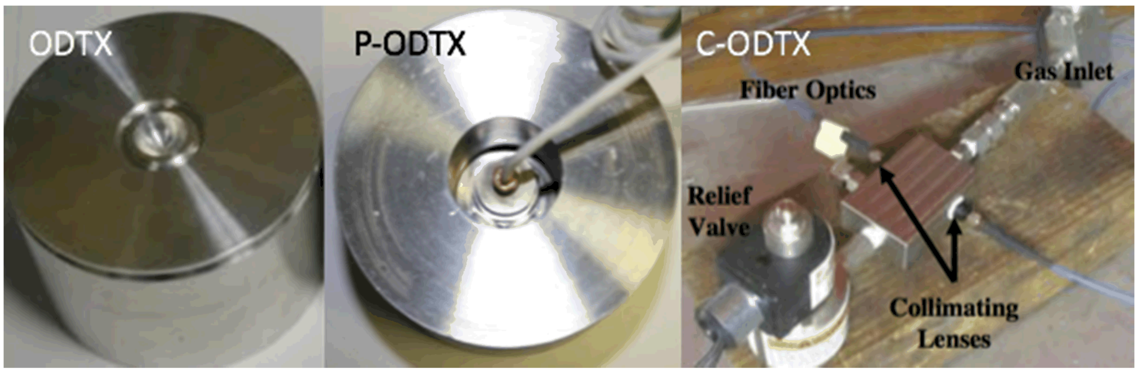

FIGURE 1. Left side: ODTX anvil sample holder; middle: P-ODTX modification, back side of anvil; right side: C-ODTX gas sample cell and connection site

Sampling Modifications to the ODTX System. Figure 1 left side shows examples of the anvils in used in the ODTX experiment. The sample fits directly into cavity of the center of the anvil. Two anvils of mirror design are compressed together to confine the sample. Figure 1 middle shows the opposite side of the upper anvil where the modifications are made for the P-ODTX system. In this view of the center of the anvil, high pressure tubing is connected. The other end of the tubing connects to a pressure transducer. The pressure transducer range is chosen based on the anticipated high-pressure limit of the experiment. For some thermal damage experiments, the system is not taken to explosion. Figure 1 right side shows the current modification for C-ODTX. This configuration uses the same high-pressure connection used in the P-ODTX experiments, but instead of connecting to a pressure transducer, the other end of the tubing connects to the optical cell at the gas inlet on the far right. Fiber optics used for the spectroscopy (IR detection) are connected to the cell on the sides.

Optical Test Cell and Detection. The cell incorporates fused-silica collimating lenses, a pressure transducer, and a thermocouple which are all threaded and sealed with Torr-Seal, a high-pressure sealant. The lenses are 6 mm diameter, aligned directly opposite each other with a 50-mm gap as the optical path-length. The assembly is rated up to 15,000 psi at ambient temperature with no observed leaks. A high-resolution FT Near-IR (NIR) spectrometer (Bruker, Matrix F) is used to collect the spectra from the 4000-6000 cm^{-1} (1666–2500 nm) with 0.5 or 4.0 cm^{-1} resolution. The internal light source uses a 20 W tungsten-halogen bulb and low-OH fused silica fiber optics (600 μm diameter, Polymicro Technologies, Inc.) are used to couple the light to and from the lenses in the test cell. Spectra are obtained by averaging 32 scans at a 40-kHz scan rate with boxcar apodization.

3. RESULTS

3.1 ODTX

Time to Explosion of LLM-105. Figure 2 shows ODTX data of several lots of LLM-105, PETN, RDX, HMX and TATB. The data show the thermal sensitivity of LLM-105 falls between that of HMX and TATB. Lot MZ6-28-5 of LLM-105, made from the DAPO process, was examined at 59% TMD (powder), and 83% and 93% TMD (both pressed), and exhibited some differences in thermal sensitivity based on density. Lot C-813 of LLM-105 at 52% TMD, recrystallized from Lot C-720, exhibited an one-order of magnitude improvement in thermal sensitivity upon recrystallization. The higher sensitivity of Lot C-720 is probably due to the presence of volatile impurities[9]. Ultrafine TATB (fluid energy mill grind) and Lot C-635 of LLM-105 demonstrate particle size effect on time to explosion. The finer materials are more reactive compared to the corresponding coarser materials at some temperatures. The larger surface area of the finer particles allowed for gaseous reactions to proceed faster than coarser particles when thermal decomposition process commences. HMX has also shown a similar behavior[4].

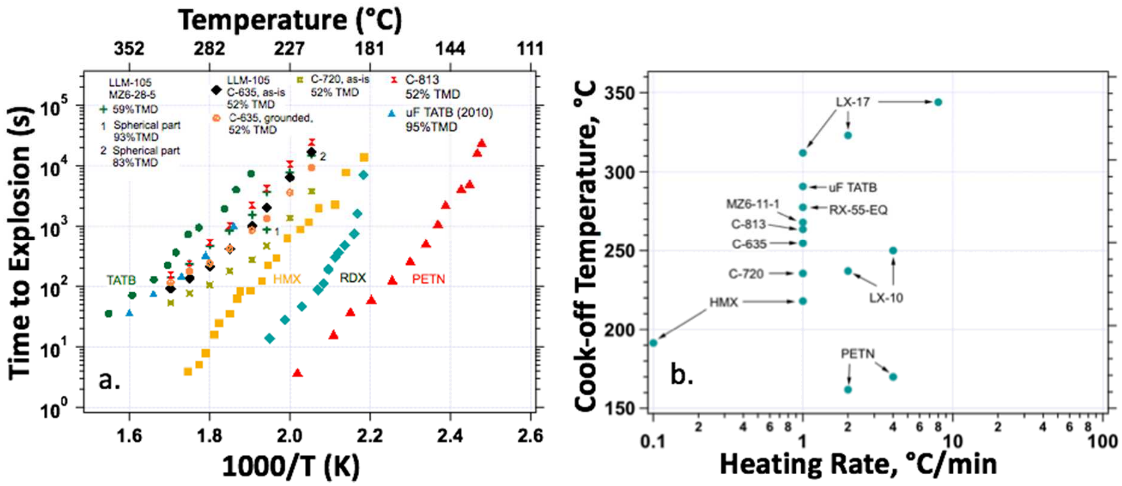

FIGURE 2. a) time to thermal explosion (ODTX) determined isothermally at different temperatures for several preparations of LLM-105 compared to selected standard materials; b) cook-off temperature as a function of heating rate for several materials

Critical temperatures for thermal explosion have been derived from these measurements. For a 0.5-in spherical part, the values are, in °C: PETN, RDX, HMX, LLM-105, TATB; 120, 170, 175, 190, 220, respectively. LLM-105 ranks more stable than HMX, RDX and PETN.

Explosion Violence of LLM-105. In the ODTX experiment, after thermal explosion, the spent anvils were scanned for cavity volume increase. This increase can be correlated to the degree of violence of the explosion[8], and gives a relative value as measured against well-characterized standards. LLM-105 had a very small cavity volume increase of 0.09 cc/g or a relative degree of violence of 0.06. For reference, LX-17 (TATB based) and PBX-9501 (HMX based) have cavity volume increases of, cc/g: 0.07 and 2.50, respectively; relative degree of violence, 0.05 and 1.60, respectively. The LLM-105 has a very low relative degree of violence, close to the degree of violence of TATB.

3.2 P-ODTX

Cook-off Temperature at Different Heating Rates. P-ODTX tests were performed on various energetic materials at different heating rates with pressure and thermal explosion temperatures recorded. Figure 2b shows cook-off temperature vs. heating rate for various energetic materials. Cook-off temperature is a function of material, heating rate, geometry, particle size and density (porosity). Fast heating results in higher cook-off temperatures. The data offer an opportunity to construct predictive cook-off models for thermal safety assessment of systems that use the energetic material. Table 1 describes the materials and test data. P-ODTX system has been used extensively to determine cook-off temperature and gas pressure at 1 °C/min heating rate on various batches of LLM-105 and their formulations during the scale-up production process. Note the changes in cook-off temperature of the preparations of LLM-105 before and after purifications. Monitoring this variation is critical in affirming materials to meet specifications and requirements.

Pressure Production during Thermal Heating of LLM-105. When an energetic material is heated in a confined space, pressure increases slowly at low temperature. As the temperature increases, thermal decomposition accelerates resulting in higher gas pressure until thermal explosion occurs, at which time gas pressure increases very rapidly, often exceeding the seal pressure of the ODTX system (30,000 psia). The P-ODTX monitors gas pressure to right before thermal explosion, an important set of data for the validation of cook-off models.

Figure 3 left side shows the gas pressure evolution behavior of LLM-105 (Lot C-864) powder when heated at 1 °C/min until thermal explosion occurred at 257 °C. Gas pressures increased to 71 bars (1130 psia), as this is the highest pressure obtainable with a conventional gas-measuring configuration. Figure 3 on the right side is rapid-response monitoring with a scope, in µsec, for the same experiment right before explosion. The gas pressure is neatly resolved as it increased from 200 bars to 2000 bars in 200 µsec before thermal explosion.

Table 1. Cook-off temperature at different heating rates

Sample description	Rate, °C/min	Cook-off temperature, °C
LLM-105, Lot C-720, DAPO process, before purification	1	235.5
LLM-105, Lot C-813, DAPO process, after purification	1	263.7
LLM-105, Lot C-635, DMP process, before purification	1	254.7
LLM-105, Lot MZ6-11-1, DMP process, after purification	1	268.1
RX-55-EQ, 94% LLM-105, MZ6-11-1, 6% binder	1	277.6
PETN, packed powder	2	162.0
PETN, packed powder	4	170.0
HMX, packed fine powder	0.1	191.4
HMX, packed fine powder	1	218.0
LX-10, pressed part	2	237.0
LX-10, pressed part	4	250.0
ultra fine (uF) TATB, packed powder	1	290.8
LX-17, pressed part	1	312.0
LX-17, pressed part	2	323.0
LX-17, pressed part	8	344.0

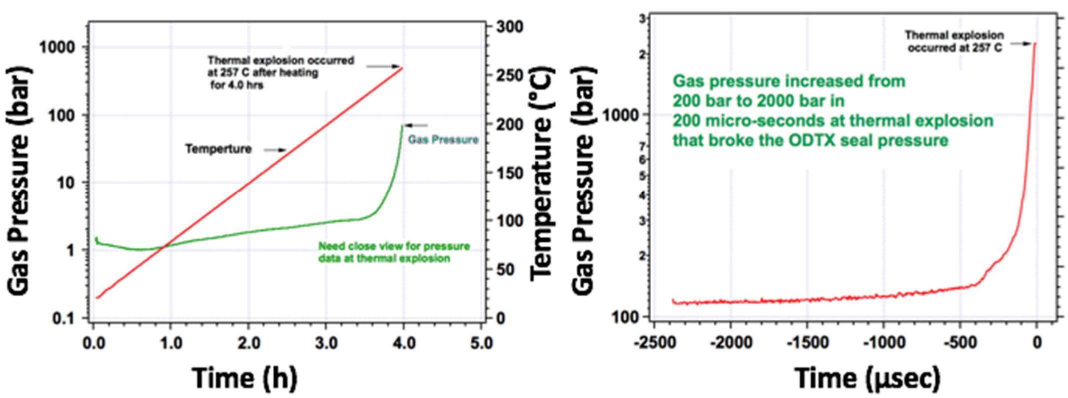

FIGURE 3. Pressure response of LLM-105 during P-ODTX thermal experiment at a 1 °C/min heating rate; left-side: overall pressure behavior; right side: high resolution rapid-recorded pressure within µsec of explosion

3.3 C-ODTX

The C-ODTX modifications are in the initial phase. Testing of the optical cell shown in Figure 1 right hand side is the current focus. This cell is connected to the ODTX system through the pressure monitor connection. The new configuration will have the pressure transducer connected such that both pressure and gaseous monitoring will be routine.

Gaseous species calibration. CO_2 is the main calibration gas for the C-ODTX. The absorption spectrum shows overtones and combination bands (Fermi triad). Absorption follows Beer's law and the response increases linearly with concentration. Under variable pressure, baseline absorption measurements showed a wavelength dependent increase. No molecular absorption features were observed and the wavelength dependence is consistent with the wavelength dependent refractive index of air as reported previously[11]. The range from 5170-4750 cm^{-1} is used for quantitative analysis.

Figure 4 left side shows a series of spectra of CO_2 measured in the cell after adding dry ice and increasing the pressure up to 5000 psi with the house air. These spectra have been baseline normalized and adjusted for baseline-pressure offset. Some band broadening was observed at the pairs of bands around 5100 and 4850 cm^{-1} while the maximum at 4950 cm^{-1} appears to be decreasing in intensity and splitting with increasing pressure. While the splitting is not totally understood at this point, it may be due to interactions with residual water vapor forming carbonic acid. This is currently under further investigation.

Figure 4 right side shows the NIR spectra of selected gases of interest in C-ODTX. N_2O and CO also have absorption bands in the NIR spectral range and are readily observed. The small, highly resolved bands in the CO spectrum near 5500 cm^{-1} are due to water vapor overlap.

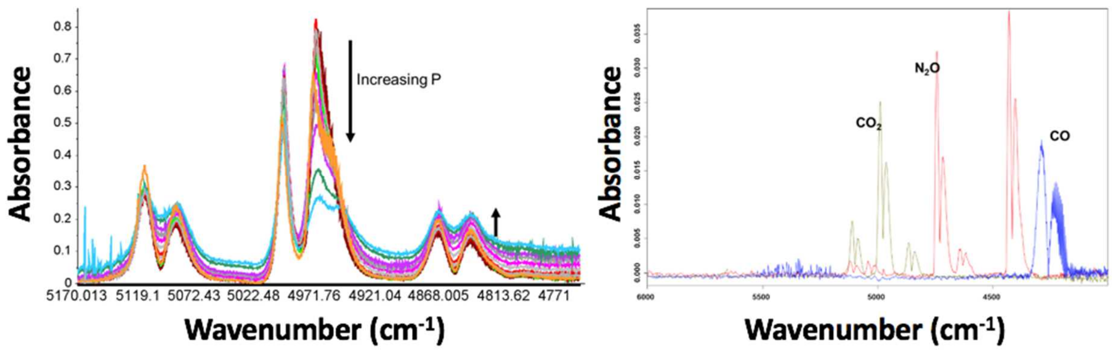

FIGURE 4. NIR spectra with optical cell; right side: CO_2 absorption spectra at several pressures up to 5000 psia at 0.5 cm^{-1} resolution; left side, selected gases of interest to thermal degradation in ODTX.

4. SUMMARY

The thermal behavior of several preparations of LLM-105 has been characterized by ODTX. The thermal sensitivity is between HMX and TATB. The pressure behavior has also been characterized by P-ODTX for many energetic materials, demonstrating, for the first-time, direct gas pressure measurements in μsec intervals during a thermal explosion. These cook-off temperature measurements have been used extensively for the scale-up of LLM-105. Progress has been made in development of C-ODTX. NIR spectroscopy is capable of detecting many gases of interest in the ODTX experiments and the components can perform at the high temperatures and pressures required. The simple interface allows for in-situ measurements which will not alter the chemistry of the head-space.

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