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Effect of Pressure on TATB and LX-17 Thermal Decomposition

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Abstract: Thermal decomposition of TATB (1,3,5-triamino-2,4,6-trinitrobenzene) and its formulation LX-17 is studied at pressures from 0.1 to 7 MPa for both isothermal heating at 340 K and ramped heating at 1 to 6 K min⁻¹. Conditions that eliminate self-heating are thoroughly explored to avoid experimental artifacts. The increase in pressure accelerates the rate of decomposition by only about 10%, but it substantially increases the enthalpy of the reaction, presumably because of longer volatile product residence times in the heated zone. The narrowness of the decomposition profile and the acceleratory phase during isothermal pyrolysis are consistent with a multistep autocatalytic mechanism, and the lack of a significant pressure effect suggests that the autocatalytic species have low volatility.

1. Introduction

The thermal initiation of energetic materials is a concern in accidents, where unintended ignition can result in an explosion. These thermal initiation mechanisms are highly complex and often depend on multiple variables including heating rate, confinement, and pressure. In a fuel fire, for example, an explosive component may be heated over timescales of minutes to hours, and many of these variables can influence the outcome.¹ An accurate chemical kinetic decomposition model is helpful for assessing the impacts of thermally induced explosions in such situations.² One aspect of a reliable model is its pressure dependence, because autocatalytic reactions characteristic of thermal decomposition of energetic materials are typically accelerated by pressure.

TATB (1,3,5-triamino-2,4,6-trinitrobenzene) is an insensitive explosive that is particularly useful because of its high thermal stability. There are a wide range of chemical kinetic measurements and models for thermal decomposition of TATB in the literature,^{2,3,4,5,6,7,8,9,10,11,12,13,14} but few address the effects of pressure. This paper pursues a very specific objective, which is to assess whether hydrostatic pressure has an important effect on the rate of the TATB decomposition at both isothermal and ramped heating conditions. This objective does not include exploration of the chemical mechanisms behind the effect or extension of the results to explosion/detonation phenomena. Rather, this study strives to highlight the pressure effect as the necessary aspect in

the development and testing of thermal decomposition models. Considering the effect of pressure helps identify dominant mechanisms and construct a global mechanism that will work over a wide range of conditions.

2. Experimental Section

2.1. Samples

The TATB used in this work has an approximate purity of 98% as measured by HPLC.¹⁵ LX-17 is a plastic bonded explosive consisting of 92.5 wt. % TATB and 7.5 wt. % Kel-F. Kel-F is a 3:1 copolymer of chlorotrifluoroethylene and vinylidene fluoride.

2.2. Thermal Analysis Methods

Thermal analysis was performed at the University of Alabama at Birmingham. The samples were used as-is from the vials provided by LLNL. The average required mass for each sample at each heating rate was determined based on calculations to reduce sample self-heating. The masses of LX-17 and TATB were ~ 0.20 mg and ~ 0.30 mg, respectively. Minimizing mass is the necessary condition for obtaining the intrinsic decomposition kinetics, which is unaffected by heat transfer.^{16,17} Note that for the studies related to the explosion phenomena much larger masses are used because heat transfer lies in the essence of this phenomenon.

The samples were individually loaded into a 40 μ L Al pan and sealed with a 0.9 mm pierced lid. The pierced lid was needed to suppress the sublimation of TATB prior to decomposition, especially at atmospheric pressure. Indeed, under such conditions we could not detect any endothermic signal preceding the decomposition exotherm. A Mettler-Toledo heat-flux HP DSC 1 module was used to measure the decomposition under 0.1 MPa (1 atm) and up to 7 MPa (70 atm) of pressure under both isothermal and non-isothermal conditions. The 7 MPa limit is based on the pressure available in purge-gas bottles.

The heating method used for non-isothermal measurements for both samples was from 250 °C to 425 °C at 6, 2.5, and 1 K min⁻¹. The samples were also run isothermally at 340 °C for 60 min. The isothermal temperature was reached in two steps, first from 100 °C to 336 °C at 10 K min⁻¹, followed by a slower heating rate of 336 °C to 340 °C at 2 K min⁻¹. Upon loading a sample in HP DSC, the pressurized chamber was purged for 3 min with nitrogen at a flow rate exceeding 200 mL min⁻¹ to ensure all atmospheric air was removed from the chamber. Next, the chamber was pressurized by nitrogen to 0.1, 1.0, 3.5, or 7.0 MPa. The 3.5 MPa pressure was used only in preliminary experiments exploring self-heating. All runs were carried out in duplicate to ensure repeatability. The temperature, heat flow, and τ -lag calibrations were performed using In and Zn melting point standards at each pressure individually. Enthalpies were calculated from the integral of the DSC curves after making a baseline correction.

3. Results and Discussion

3.1. Self-heating observations

When an energetic material decomposes during constant heating-rate experiments, the sample temperature rises significantly above the desired ramp temperature. The experiment can exceed the ASTM guideline¹⁸ of 8 mW for the maximum heat flow from an energetic material DSC run. Extreme cases lead to a profile where the sample temperature cools after the maximum heat release for a ramped heating experiment in which the furnace temperature is still rising. LX-17 was much more prone to this self-heating problem than TATB. Postulates for this observation include reduced heat removal from the sample due to the thermal insulating character of Kel-F and reduced diffusion of gaseous autocatalytic species from the sample. The precise reason is not understood.

Figure 1 shows that the difference between the measured sample temperature and the reference temperature correlates well with the maximum heat flow from the sample. Data from a variety of heating rates and pressures of 3.5 and 7.0 MPa are included in this plot. The 8 mW ASTM limit is achieved for a temperature difference of about 0.5 K. Although the melting point calibration approximately corrects for the nonzero thermal gradient between the sample and the sample thermocouple, the true sample temperature is larger by an unknown and possibly substantial amount when self-heating becomes large. That issue raises significant concerns for kinetics experiments, for which true sample temperatures must be known to within 1 °C for accurate determinations.¹⁹

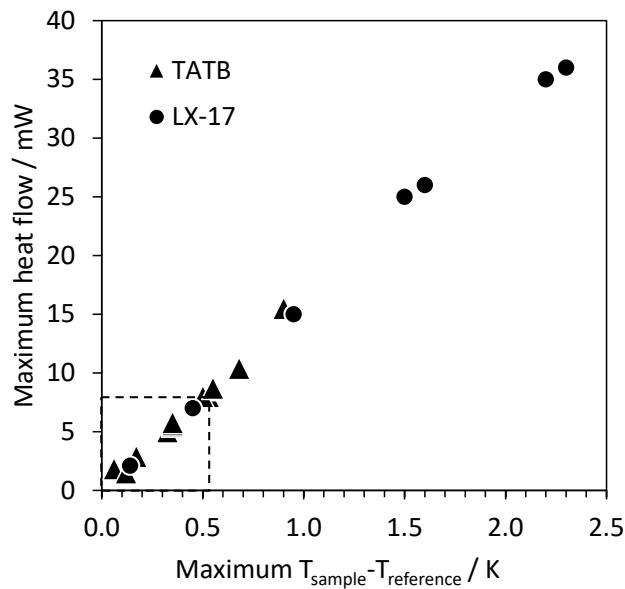


Fig. 1. Relationship between the maximum heat flow and the maximum difference between the sample and reference thermocouples for selected measurements on TATB and LX-17.

Figure 2 shows that the product of the sample size and heating rate cannot exceed approximately 4 mg·K min⁻¹ for self-heating to be within control bounds. Even below that value, sometimes LX-17 undergoes thermal runaway. This observation confirms and even strengthens previous recommendations^{16,17} that when characterizing energetic materials, the sample size must be very small, and even then, the results should be checked to make sure unacceptable

self-heating has not occurred. This result also points out that the common procedure in thermal analysis to keep the sample size the same at all heating rates is not a good idea for samples with large exothermic or endothermic enthalpies. Instead, the sample size should vary inversely with the heating rate to maintain a good thermal analysis signal without excessive self-heating.²⁰ It is important to understand that this criterion is different from the design of experiments where self-heating is part of the phenomenon being studied, as is the case with experiments exploring the conditions of thermal ignition.

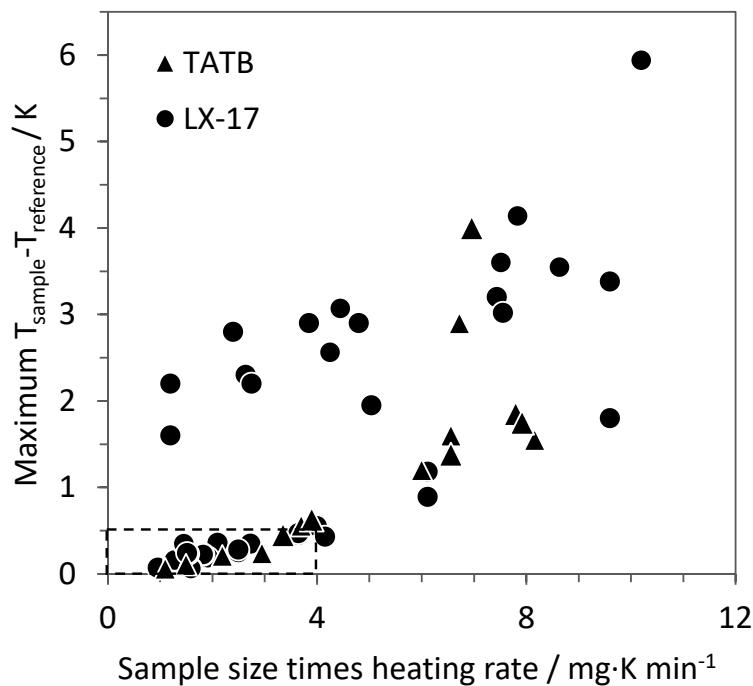


Fig. 2. The relationship between self-heating and the product of the sample size and heating rate for selected measurements on TATB and LX-17.

3.2. Effect of Pressure

Figure 3 shows the effect of pressure at various heating rates for TATB. The effect on LX-17 (not shown) is similar. The reaction profile shifts slightly to lower temperature by an average of 1 K when pressure is increased to 7 MPa. Similar results were obtained in an earlier LLNL study.¹⁴ At atmospheric pressure, the enthalpy for TATB clearly increases with heating rate. A less pronounced increase occurred for LX-17 (not shown). At a constant heating rate of 6 K min⁻¹, the enthalpy increases with pressure for both TATB and LX-17. These pressure trends are shown in Figure 4. This increase is likely due to more complete gas-phase decomposition reactions in the headspace due to the longer residence time. However, the additional decomposition could also be occurring in the solid phase due to increased solubility of gaseous products, slower diffusion out of the solid,²¹ or both.

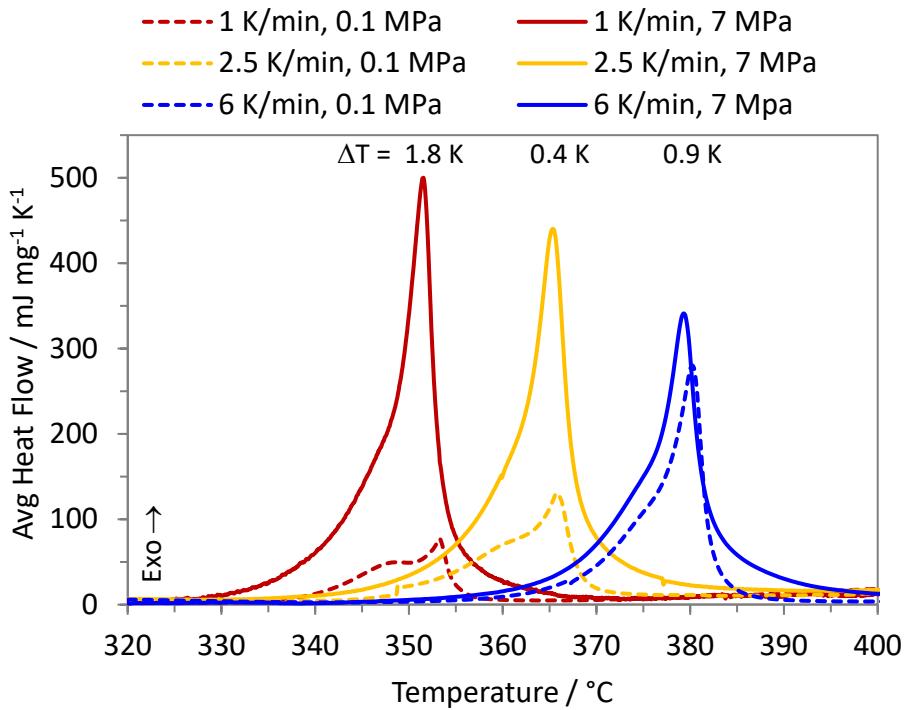


Fig. 3. Exothermic thermal decomposition profiles for TATB heated at 1, 2.5, and 6 K min⁻¹ at 0.1 and 7 MPa. The heat flow is scaled by heating rate to make the profile areas directly proportional to the total heat release.

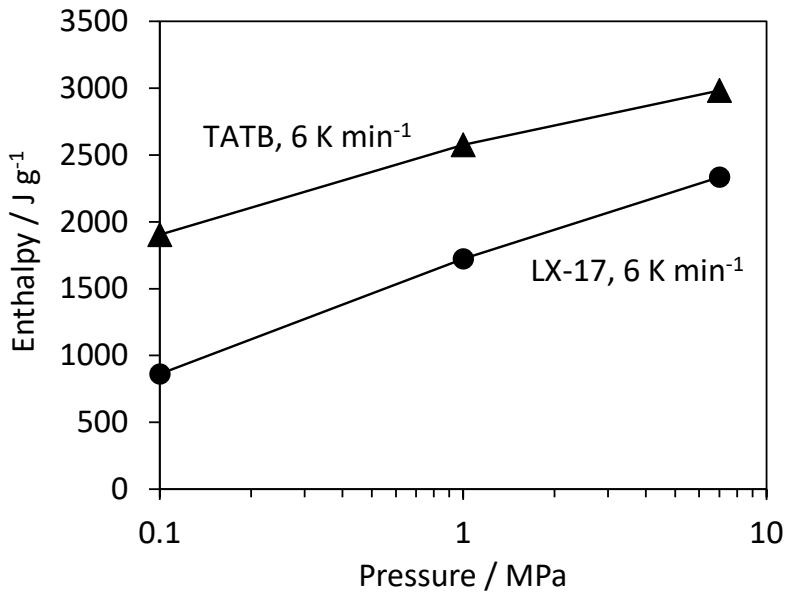


Fig. 4. Enthalpy of TATB and LX-17 as a function of nitrogen gas pressure. The lines simply connect the data points.

Figure 5 shows the thermal decomposition rates and reaction profiles of both materials measured at 340 °C. The reaction profile for LX-17 at 7 MPa was remeasured after an earlier preliminary report²² of these and other results due to an unexpected large difference between the 1 and 7 MPa reaction profiles. The reaction enthalpies are more difficult to quantify in this case due to baseline uncertainties, but the approximate values for both materials increase from 900 to 1350 to 1900 J g⁻¹ as pressure increases over this range. This may be due to more complete reaction of volatiles in the pan headspace, given that the residence time in the pan headspace is inversely proportional to pressure.

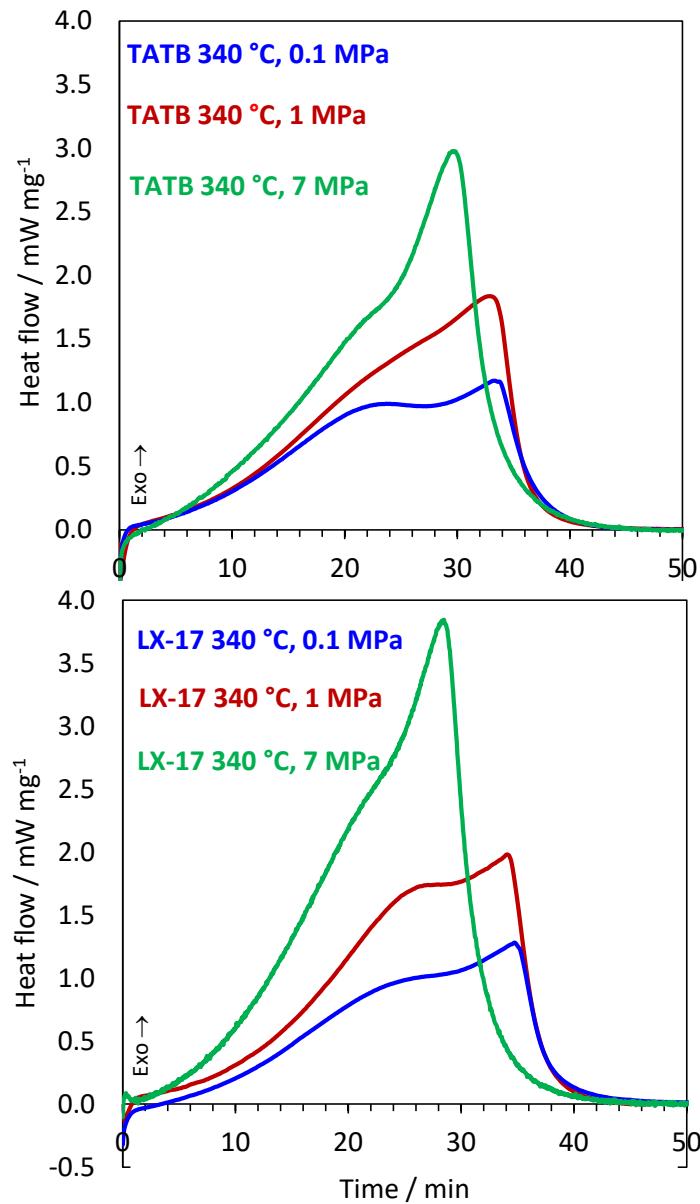


Fig. 5. Thermal decomposition of TATB and LX-17 at 340 °C and nitrogen gas pressures of 0.1, 1, and 7 MPa.

3.3. Chemical kinetic observations

The thermal decomposition of TATB is a complex multistep process, and only a qualitative kinetic analysis of heat release is reported here. Two reaction components (the main peak and a leading shoulder) are visible in both isothermal and ramped heating experiments. Rigorous kinetic analysis results were sensitive to baseline assumptions, which limits our ability to report a quantitative kinetic model.

In the ramped heating measurements, the separation between the two processes is most visible at 1 K min^{-1} and 0.1 MPa (see Figure 3). The two processes tend to merge as heating rate increases, which implies a lower activation energy for the first reaction. However, the enthalpy also increases substantially as heating rate increases, so part of the merging may be due to more complete secondary reactions. That increase would violate the basic assumption behind an isoconversional kinetic analysis. In addition, the very sharp peak in combination with the slight shift in temperature leads to substantial standard errors.

Kissinger's method²³ yields $A = 8.47 \times 10^{14}\text{ s}^{-1}$ and $E = 214.4\text{ kJ mol}^{-1}$. The standard deviation in E is only 4.3 kJ mol^{-1} , but that precision likely underestimates the potential errors due to systematic errors, assumptions of a first-order reaction,²⁴ and the change in the mix of reactions and possibly more self-heating at higher heating rates due to more complete reaction. The second peak is much narrower than a first-order reaction, which indicates an autocatalytic reaction.^{25,26}

At 7 MPa , the first component is an indistinct shoulder on reaction profile. That is in part because the second peak has decreased slightly in temperature. Both differential and integral isoconversional analysis²⁶ indicated the activation energy was in the $200\text{--}210\text{ kJ mol}^{-1}$ range during most of the reaction. Kissinger's method gave $A = 5.07 \times 10^{13}\text{ s}^{-1}$ and $E = 207.6 \pm 1.9\text{ kJ mol}^{-1}$. However, the reaction profile was only 27% as wide as a first-order reaction, which again suggests a highly autocatalytic reaction, especially since the profile was broadened by a low temperature shoulder.

The isothermal reaction profiles in Figure 5 confirm that the reaction is most likely autocatalytic due to its acceleratory character, i.e., the reaction rate initially increases with time after reaching isothermal conditions rather than decrease with time as it would for a deceleratory reaction (e.g., a first-order reaction). This is consistent with earlier conclusions. The mean activation energy of about 210 kJ mol^{-1} is within the range of reported values.^{8,9,10,11} We suspect that reported activation energies significantly higher than 210 kJ mol^{-1} are influenced by self-heating and should not be considered reliable.

For instance, a widely cited high activation energy is 251 kJ mol^{-1} from Rogers⁷ appears rather problematic. Unfortunately, Rogers has not reported the sample masses, or heating rates, or presented the DSC data in his paper. This makes it impossible to estimate the extent, to which the reported activation energy could be affected by self-heating. Yet, it is worth noting that the excessive value can be readily determined at relatively minor self-heating. Assume that we do two experiments—one at 1 K/min and one at 6 K/min . For $A=1\text{e}15\text{ s}^{-1}$ and $E=210\text{ kJ/mol}$, the first-order T_{\max} values are 338.1 and $364.4\text{ }^\circ\text{C}$, respectively. Now consider the case where the sample temperature is 1 K hotter than the sample thermocouple at 1 K/min and 5 K hotter at 6 K/min . As seen from Figure 2,

these are entirely realistic superheatings. That means when the sample has reached the true T_{\max} values above, the sample thermocouples will read only 337.1 and 359.4 °C, respectively (the sample is hotter because it is exothermic). If we use those apparent sample temperatures for the kinetic analysis, Kissinger's method gives $E=247$ kJ/mol, which is practically the same as the value reported by Rogers.

In contrast to HMX, pressure has a relatively minor effect on the reaction rate of TATB. This is consistent with one earlier report.¹⁴ For an activation energy of about 210 kJ mol⁻¹, the approximately 1 K downward shift of the constant heating-rate experiments corresponds to a 6% increase in reaction rate. From the change in the peak reaction time, the isothermal results in Figure 5 suggest more like a 15% increase in reaction rate for TATB and a little more for LX-17. Averaging the isothermal and nonisothermal results, the rate increase can be estimated as roughly 10%. In contrast, the $P^{0.3}$ pressure coefficient for HMX indicates a 3.6-fold acceleration at 7 MPa.²⁷ The difference between HMX and TATB suggests that the autocatalyst for HMX is gaseous, whereas it is non-volatile for TATB.

4. Conclusions

The decomposition of TATB and its formulation LX-17 are mildly accelerated by pressure by about 10% at 7 MPa, given an average among the ramped and isothermal heating experiments. The principal apparent activation energy is about 210 kJ mol⁻¹ and is not changed within measurement accuracy. Pressure also increases the enthalpy from below 1000 J g⁻¹ for slow reaction times at atmospheric pressure to approximately 3000 J g⁻¹ for decomposition at 7 MPa over several minutes. This must be due to more complete decomposition related to the longer confinement times at elevated pressures. The overall reaction profile clearly has at least two decomposition steps, and more complex chemical kinetic modeling is needed to describe the reaction profile well.

Acknowledgments and Disclaimers

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