# Thermal Properties of FOX-7

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## INTRODUCTION

Much effort has been devoted to an ongoing search for more powerful, safer and environmentally friendly explosives. Since it was developed in the late 1990s[1], 1,1-diamino-2,2-dinitroethene (FOX-7), with lower sensitivity and comparable performance to RDX, has received increasing interest. Preliminary results on the physical and chemical characterization of FOX-7 have shown that it possesses good thermal and chemical stability.[1] It is expected that FOX-7 will be a new important explosive ingredient in high performance, insensitive munition (IM) explosives.[2]

One of the major focuses in research on this novel energetic material is a study of its thermal properties. Östmark et al have reported that DSC curves exhibit two minor endothermic peaks as well as two major exothermic peaks.[3] Two endothermic peaks at ~116 and ~158 °C suggest the presence of two solid-solid phase transitions. A third phase change below 100 °C has also been reported based on a X-ray powder diffraction (XPD) study.[4] The shapes, areas and observed temperatures of the two decomposition peaks at ~235 °C and ~280 °C vary with different batches and sources of the sample, and occasionally these two peaks are merged into one.[5,6] The factors leading to this variation and a more complete investigation are in progress.

Our laboratories have been interested in the thermal properties of energetic materials characterized by means of various thermal analysis techniques. This paper will present our results for the thermal behavior of FOX-7 including the phase changes, decomposition, kinetic analysis and the decomposition products using DSC, TG, ARC (Accelerating Rate Calorimetry), HFC (Heat Flow Calorimetry) and simultaneous TG-DTA-FTIR (Fourier Transform Infrared Spectroscopy)-MS (Mass) measurements.

## EXPERIMENTAL

FOX-7 (1,1-diamino-2,2-dinitroethene) used for ARC, HFC and TG-DTA-FTIR-MS analysis was obtained from NEXPLO Bofors AB; For DSC measurements it was synthesized at Lawrence Livermore.

DSC measurements were conducted using a TA Instrument model 2920 Differential Scanning Calorimeter and hermetically sealed aluminum pans with pinholes in the lids. Sample sizes were approximately 0.5 mg. TA Instruments model 2960 TG-DTA and open aluminum pans have been employed to measure weight loss. Approximately 0.5 mg decomposed at heating rates from 0.1 to 1.0 $^{o}$C min$^{-1}$. Degradation was carried out under nitrogen carrier gas at a flow rate of 100 cm$^3$ min$^{-1}$.

A modified SETARAM C-80 instrument was used for a HFC study on thermal decomposition of FOX-7. About 50 mg of FOX-7 was placed in an alumina liner which was loaded into a stainless steel vessel. An equivalent mass of sapphire was used as the reference material. The experiments were conducted at ambient and 8.85 MPa argon pressure and a heating rate of 0.3 °C min$^{-1}$ in a temperature range of 28 to 300 °C.

The ARC measurements were performed on a Thermal Hazard Technology instrument to evaluate the thermal stability of FOX-7. A lightweight spherical titanium vessel was employed for the sample container. The isothermal experiments were carried out in a closed system and set to run at 200 °C and 210 °C respectively in argon.

TG-DTA-FTIR-MS was applied to study the thermal behavior and identify the volatile products formed in the course of the experiment. A simultaneous TG-DTA 2960 module was interfaced to a Boman MB100 FTIR and a Balzers Thermostar GSD300 Quadrupole MS. The experiments were performed in helium and in air with 5 mg of FOX-7 at a heating rate of 5 °C min$^{-1}$. An isothermal study with the same sample size was conducted at 190, 195, 200 and 205 °C in helium with a flow rate of 100 cm$^3$ min$^{-1}$.


## RESULTS and DISCUSSION
### Solid phase transition study by DSC

The three solid-solid phase transitions prior to chemical decomposition are summarized in Table 1. The first transition ($\alpha \rightarrow \beta$) is a second-order monoclinic-orthorhombic transition that occurs over the temperature interval of 75-95 $^{o}$C, but it is not visible by DSC. Consequently, we determined kinetics only for the second two solid-solid phase transitions by DSC. An endotherm was reported earlier by Jones et al.[7] for FOX-7 over the 75-95 $^{o}$C interval in a Heat Flux Calorimeter (HFC), which uses 50 mg sample sizes. However, that endotherm did not appear for thermally cycled samples and was therefore attributed to impurities.

**Table 1.** Summary of phase transformation information from Bemm and Eriksson[5]

| phase | formation T | notes |
|---|---|---|
| α |  | monoclinic, P2(1)/n, d = 1.91 g cm$^{-3}$ |
| β | ~ 85 °C | orthorhombic, 4.3 % volume increase from α |
| γ | ~115 °C | formed directly from α at high heating rates |
| δ | ~155 °C |  |

Kinetic characteristics of the phase transitions are illustrated in Figures 1 and 2, which show the endotherms and exotherms for a first heating through the γ phase to the δ phase, a cooling and reversion to the α phase, and a second heating to the γ and δ phases. The largest uncertainty in the phase transformations is whether the broad feature that sometimes occurs during cool down in the vicinity of 150 °C is a reversion from δ to γ or merely a baseline problem. It is possible that the reversion at 75 °C for cooling at 3 °C min$^{-1}$ and at 50 °C at 30 °C min$^{-1}$ is a direct transformation from δ to α phase. The increase in reversion temperature with a decrease in heating rate is consistent with the previous observation of the reversion peaking at 102 °C for cooling at 0.3 °C min$^{-1}$.

A summary of the peak temperatures, $T_p$ and enthalpy values, ΔH during the β→γ and γ→δ transformations at various heating rates, r is given in Table 2. There is a small increase in the $T_p$ of the endotherm in each case. The standard deviations of $T_p$ averaged 0.25 °C for β→γ and 0.7 °C for γ→δ, so the overall increase is far greater than the uncertainty at any given heating rate. There is no obvious dependence of ΔH on r, and the average enthalpies were 21.6 J g$^{-1}$ for β→γ and 17.7 J g$^{-1}$ for γ→δ.
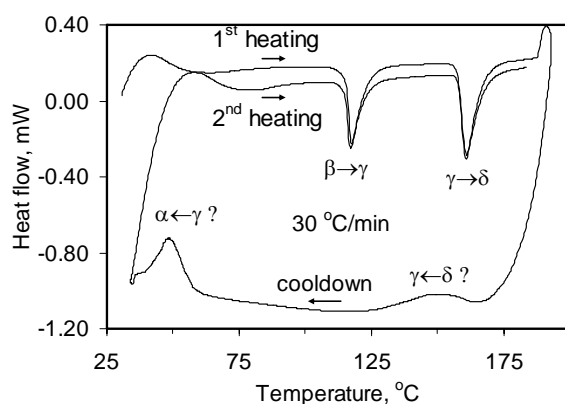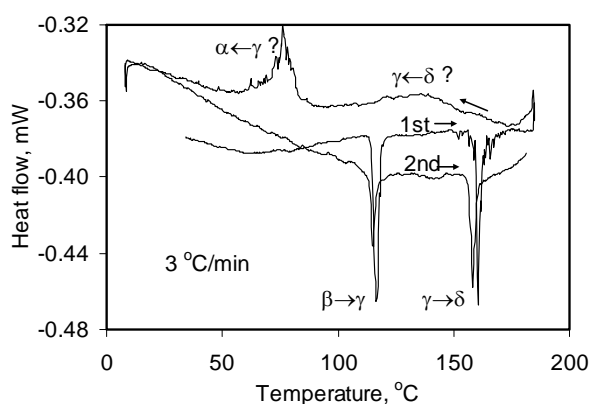


**Figure 1.** Cyclic heating and cooling of Fox-7 at 30 °C min$^{-1}$.

**Figure 2.** Cyclic heating and cooling of Fox-7 at 3 °C min$^{-1}$.

**Table 2.** Summary of phase transition data at multiple heating rates.

| | $\beta \rightarrow \gamma$ | | | $\gamma \rightarrow \delta$ | |
|---|---|---|---|---|---|
| $r/^{\circ}C\ min^{-1}$ | $T_p/\ ^{\circ}C$ | $\Delta H/J\ g^{-1}$ | $T_p/^{\circ}C$ | $\Delta H/J\ g^{-1}$ | |
| 0.1 | 114.5 | 25.3 | 158.5 | 15.0 | |
| 0.35 | 114.9 | 21.3 | 158.9 | 14.6 | |
| 1.0 | 115.8 | 18.7 | 160.4 | 16.8 | |
| 3.0 | 118.1 | 21.9 | 164.7 | 21.0 | |
| 10 | 119.7 | 21.5 | 163.8 | 18.7 | |
| 30 | 122.3 | 20.7 | 165.3 | 20.0 | |

One approach to derive kinetics for such a transformation is to use the equilibrium-inhibited Prout-Tompkins approach of Burnham et al.:[7]

$$-dx/dt = kx^n(1-qx)^m(1-1/K_{eq}) \qquad (1)$$

where x is the fraction unconverted, k is the rate constant ($k = Ae^{-E/RT}$), n is the reaction order, q is an initiation parameter, m is a nucleation-growth parameter, and $K_{eq}$ is the equilibrium constant for the transition ($K_{eq} = K_o e^{-\Delta H/RT}$). A fit to the data, shown in Figure 3, was obtained when $K_o$ and $\Delta H$ were fitted as well as the Prout-Tompkins kinetics parameters. The fit was obtained with the LLNL *Kinetics05* program. Note that the width of the transformation is underestimated at the lowest heating rate (probably because of a distribution of nucleation energies), and the induction time is underestimated at rapid heating rates. A more detailed model would be needed to fit these aspects.
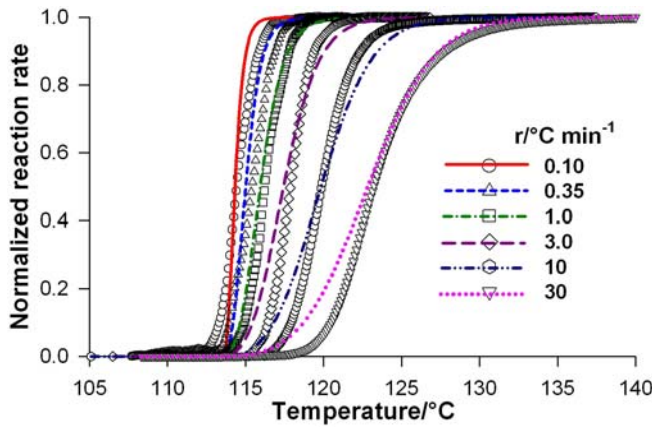


**Figure 3.** Measured and calculated fractions converted ($\beta \rightarrow \gamma$) at heating rates of 0.1, 0.35, 1.0, 3.0, 10, and 30 $^{\circ}C\ min^{-1}$ (left to right). The model parameters are $ln(A/s^{-1}) = 64.9$, E = 215.0 kJ m ol$^{-1}$, n = 1.34, m = 0.21, q = 0.999, $lnK_o = 13.1$, and $\Delta H = 42.27$ kJ mol$^{-1}$.

The back-reaction during cool down also has thermodynamic and kinetic aspects.[8] The driving force for the reversion increases in proportion to the degree of undercooling, but the rate constant decreases exponentially with temperature. Consequently, the two factors work in opposite directions for reversion, while they work in concert for conversion. This accounts for the greater dependence of the peak temperature for

reversion as a function of heating rate than for conversion. A complete kinetic model for conversion and reversion will be reported at a later date.

**Thermal decomposition study by means of DSC and TG**

There are a few previous DSC investigations of FOX-7 thermal decomposition.[5,6,7] For the most part, two exotherms are observed. However, only one exotherm is observed by de Klerk et al.[6] for a single crystal weighing 1.47 mg, and Jones et al.[7] observe only a single exotherm in a HFC using 50 mg samples. Furthermore, de Klerk et al. report a more pronounced first peak using TG and DTA for dry samples than wet samples, and Bemm and Eriksson[5] reported that the temperature of the second exotherm is higher for finer powder and for samples prebaked at 135 °C. Consequently, the kinetics of the decomposition probably depends on confinement conditions due to reactions between volatile products and remaining solid. The decomposition kinetics we report here are for heat up of sub-mg powdered samples in an open pan by TGA and in hermetically sealed pans (with pinholes in the lid) by DSC, and their generality is not yet established.

With that caveat, the peak temperatures, $T_p$ and enthalpy values, $\Delta H$ for the two peaks are summarized in Table 3. The total energy released decreases slightly as heating rate, r increases, but a more pronounced affect is that the fraction of heat released in the first peak decreases substantially as r increases. Baseline drift causes the energies to be less certain at the lowest heating rates, but the shift in energy from the first to second peak as r increases is unmistakable. The peak temperature of the first exotherm increases steadily with heating rate, and the apparent activation energy using Kissinger's method is 238.3 kJ mol$^{-1}$. The second peak is more problematic, undergoing an increase in $T_p$ from 0.1 to 1.0 °C min$^{-1}$, above which the $T_p$ is roughly constant. Kissinger's method applied to the 0.1 to 1.0 °C min$^{-1}$ data yields an apparent activation energy of 322.4 kJ mol$^{-1}$. The invariance of $T_p$ at higher heating rates could be due either to a mechanistic change related to the redistribution of heat from the second to first peak or to thermal runaway, in which the sample temperature is much higher than the measured temperature. Peak temperatures for differential thermogravimetric analysis (DTG) are also reported in Table 3 at the lowest three heating rates. They agree extremely well with the DSC peak temperatures.

Two more sophisticated methods of kinetic analysis were done: isoconversional Friedman-type analysis, and a fit to parallel nucleation-growth reactions, both using the LLNL software *Kinetics05*. Due to the agreement in $T_p$ for DSC and DTG as well as

**Table 3.** Summary of thermal decomposition data at multiple heating rates.

| r/ °C min⁻¹ | 1ˢᵗ exotherm | | 2ⁿᵈ exotherm | | total | 1ˢᵗ DTG | 2ⁿᵈ DTG |
|---|---|---|---|---|---|---|---|
| | $T_p/°C$ | $-\Delta H/$ kJ g⁻¹ | $T_p/°C$ | $-\Delta H/$ kJ g⁻¹ | $-\Delta H/$ kJ g⁻¹ | $T_p/°C$ | $T_p/°C$ |
| 0.10 | 202.3 | 1.98 | 261.7 | 0.61 | 2.59 | 201 | 260 |
| 0.35 | 210.6 | 1.20 | 271.7 | 0.99 | 2.19 | 209 | 269 |
| 1.0 | 217.3 | 1.20 | 278.6 | 1.14 | 2.34 | 217 | 277 |
| 3.0 | 226.2 | 0.85 | 277.2 | 0.96 | 1.82 | — | — |
| 10 | 238.3 | 0.52 | 274.0 | 1.40 | 1.92 | — | — |
| 30 | 249.5 | 0.52 | 278.8 | 1.39 | 1.91 | — | — |

problems getting a good DSC reaction profile at the lowest heating rate due to baseline drift, the DTG data was used to derive the kinetic parameters, and those parameters were compared to a subset of the DSC data. The nucleation-growth kinetics model is given in Table 4, and a comparison of measured and calculated reaction rates is given in Figure 4. This model was fitted simultaneously to both the reaction rate and fraction reacted, even though we show only the former. The isoconversional model parameters are shown in Figure 5, and a comparison of measured and calculated rates is given in Figure 6. The isoconversional fit is better (RSS about half as large), as would be expected, since it is essentially a 200 parameter fit rather than an eight parameter fit. The isoconversional analysis yields an activation energy that is roughly constant and equal to that obtained from the model fitting for $\alpha>0.4$. For $\alpha<0.4$ the isoconversional activation energy varies about the mean value determined from model fitting. However, it is clear from Figure 4 that a constant activation energy is not a good approximation for that reaction. Also, the isoconversional kinetic parameters are very close to those reported by Roduit et al[9] from DSC data over the same heating rate range.

**Table 4.** Kinetic parameters derived for two parallel nucleation-growth reactions from FOX-7 mass loss data.

| Parameter | 1ˢᵗ reaction | 2ⁿᵈ reaction |
|---|---|---|
| fraction | 0.422 | 0.578 |
| $\ln(A/s^{-1})$ | 50.8 | 61.5 |
| $E/kJ\ mol^{-1}$ | 219.4 | 307.8 |
| n | 3.63 | 0.31 |
| m | 0.89 | 0.00 (constrained) |
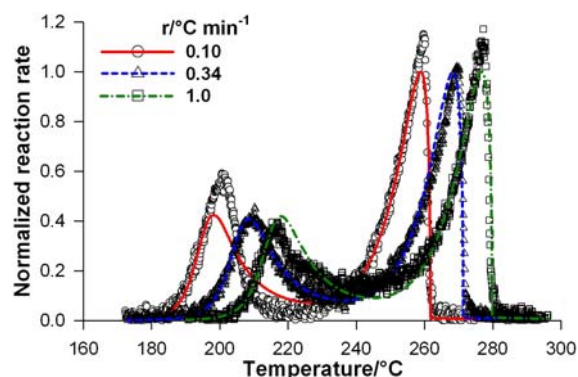


**Figure 4.** Comparison of measured and calculated rates of mass loss for FOX-7 heated at 0.1, 0.34, and 1.0 °C min⁻¹. Model parameters are given in Table 4.
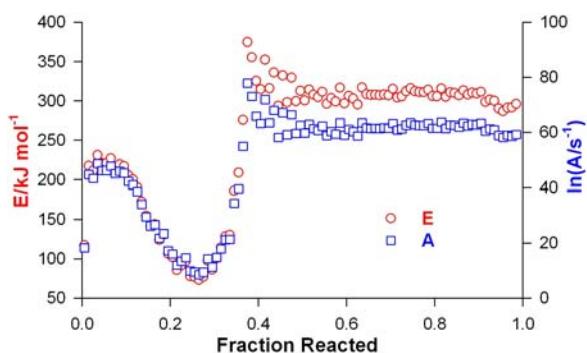
**Figure 5.** Isoconversional kinetic analysis from LLNL *Kinetics05* software.
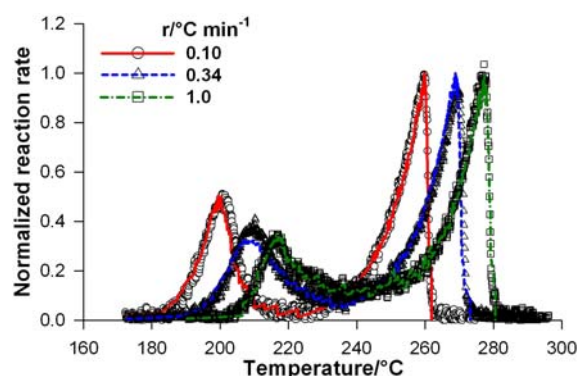


**Figure 6.** Comparison of measured and calculated rates of mass change as a function of heating rate for isoconversional kinetic analysis.

**Heat Flux Calorimetry (HFC)**

A modified heat flow calorimeter[10] was used to study the decomposition behavior of FOX-7 at ambient and 8.85 MPa argon pressure. The curve of heat flow against temperature at ambient pressure shows one sharp exothermic peak (Figure 7). The exothermic peak at 233 °C, with a $\Delta H$ = -1.65 kJ g$^{-1}$, suggests one-step decomposition under the experimental conditions used. This result is different from that observed in the DSC, which shows two exothermic peaks in this temperature range and a total larger $\Delta H$ of -2.10 ± 0.06 kJ g$^{-1}$[,7]. However, the HFC thermal curve obtained at 8.85 MPa shows two exothermic peaks with an increased total $\Delta H$ of –3.04 kJ g$^{-1}$, one large peak with a peak temperature of 239 °C and a small peak with a peak temperature of 244 °C (Figure 7). The decomposition temperature shifts to higher temperature when the system pressure was increased under the experimental conditions used. This observation suggests that pressure may be one of the factors affecting the decomposition process of FOX-7. More detailed work on the pressure effect is in progress. The two phase transitions at ~114 °C (β-γ) and ~159 °C (γ-δ) have also been detected in both runs of ambient pressure and high pressure, in agreement with the DSC results.

**Accelerating Rate Calorimetry (ARC)**

The thermal stability of FOX-7 has been investigated by the ARC technique using the heat-wait-search technique.[7] In this work, an isothermal experiment on a sample of 200 mg in argon was carried out at 200 °C, and it was set to run for 96 h in a closed system. Detectable heat release occurs after about 100 h, and sample runaway occurred at ~233 °C. When the sample size was increased to 1 g for an isothermal temperature of 200

°C, runaway was seen after 41 h due to the smaller heat loss per unit sample.  For a 1 g at 210 °C, it took 28 h for FOX-7 to attain runaway.
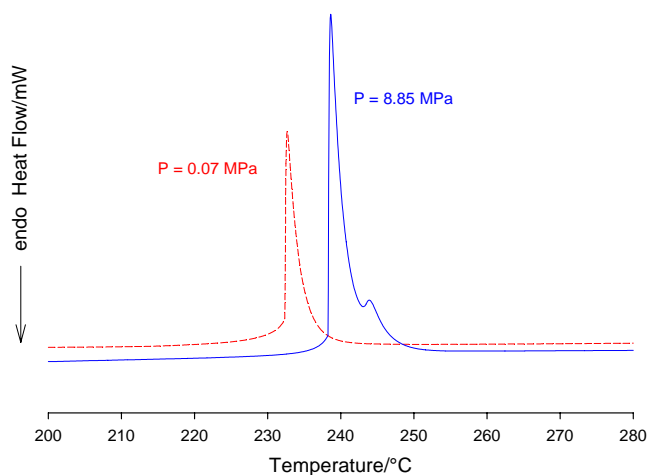


**Figure 7.** HFC study on FOX-7: 50 mg, 0.3 °C min$^{-1}$ at p = 0.07 and 8.85 MPa

## TG-DTA-FTIR-MS measurements

Simultaneous TG-DTA-FTIR-MS on FOX-7 at a heating rate of 5 °C min$^{-1}$ in helium and air has been performed and the results are compared. Both TG-TDA curves (Figure 8) obtained in helium and air exhibit two-step decomposition with a total mass loss of   83 % in helium and 93 % in air. The higher mass loss in air suggests more FOX-7 has been converted to volatile products. It is also noted that the second exothermic DTA peak is relatively larger in air than that in helium. This is probably due to the more violent reaction occurring in the second-step decomposition in air than that in helium. In addition, a minor mass loss prior to the major mass loss has been observed at a temperature of 161 °C in helium and 205 °C in air and we have assumed these mass losses are from impurities in the sample.

The FTIR results revealed that the gases, $CO_2$, HCN, $N_2O$, $NO_2$, HOCN, $H_2O$, and NO, were generated from the two decomposition steps. $HNO_2$ and HCOOH were also observed from the second decomposition step in both helium and air. More $CO_2$ and HOCN gases were evolved in the second decomposition step in air than in helium. The mass spectra data also support the observations from the FTIR experiments.

Isothermal TG-DTA-FTIR-MS experiments have been performed at 190, 200, 205, and 205 °C in helium. Figure 9 represents the results obtained from one of these experiments at 205 °C. The Figure 10 shows DTG curves at various isothermal temperatures. On the basis of regression line of ln(time of maximum DTG) vs 1/T, the initial activation energy of decomposition was estimated as 191 ± 4 kJ mol$^{-1}$ (Figure 10).
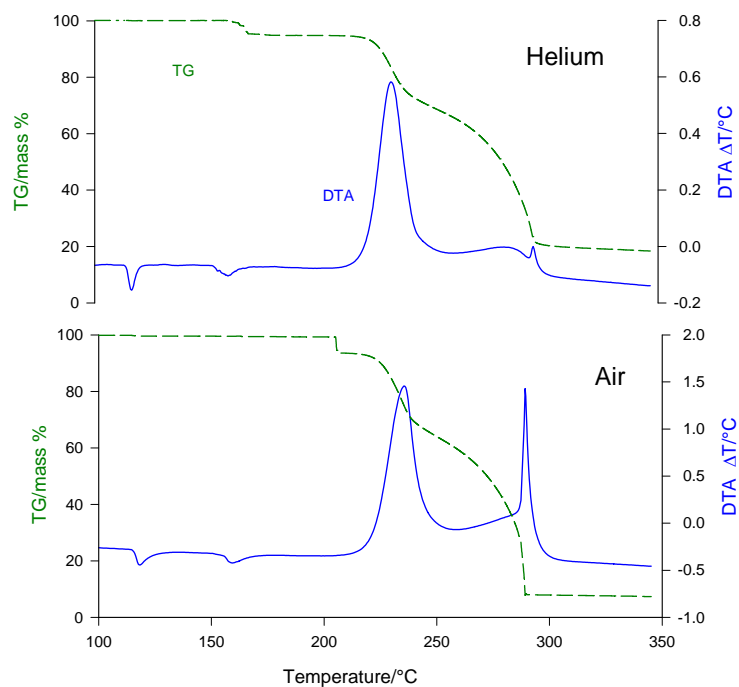
**Figure 8.** TG-DTA results for 5 mg FOX-7 heated in helium (top) and air (bottom) at 5 °C min⁻¹.
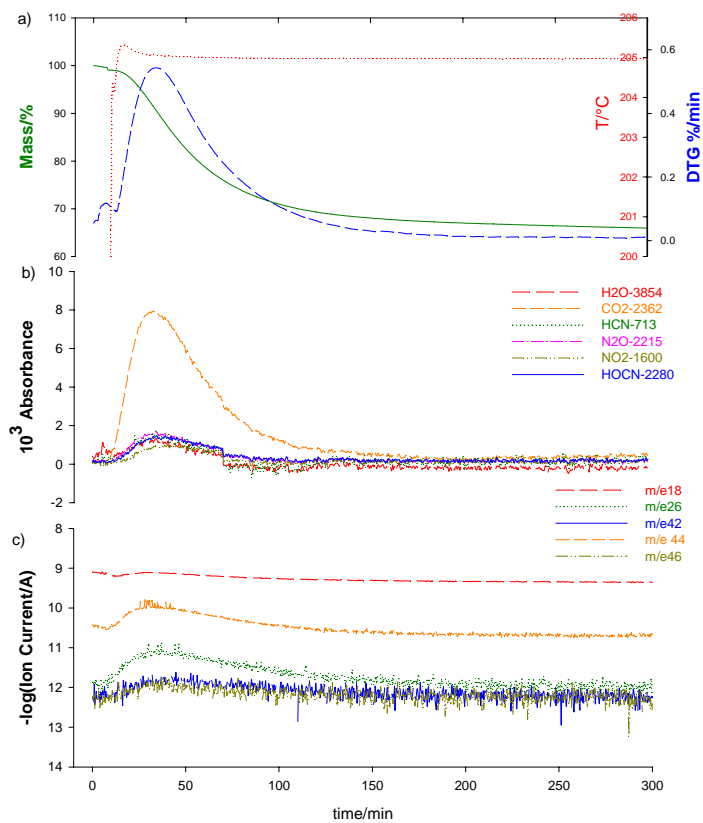


**Figure 9.** Isothermal (a) TG-DTA, (b) FTIR, and (c) MS data on FOX-7 at 205 °C
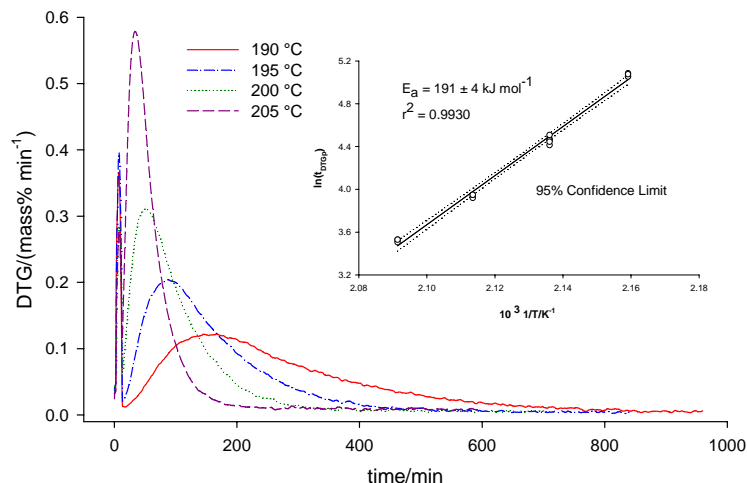
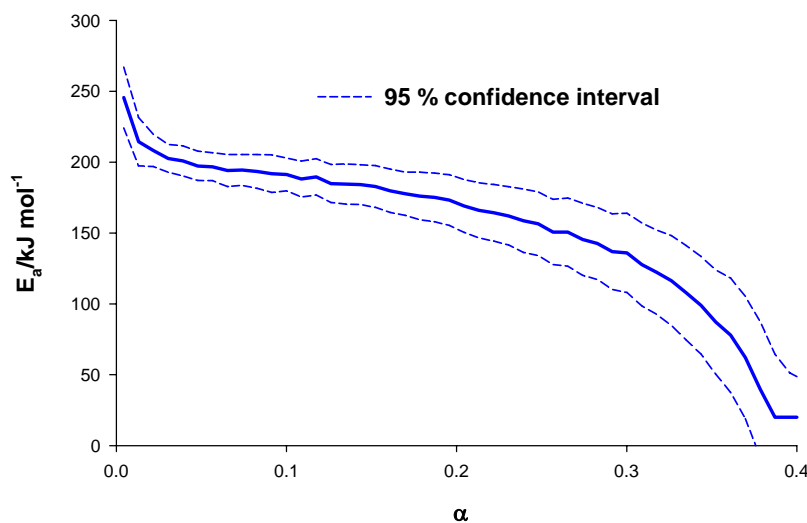**Figure 10**. Isothermal DTG curves and kinetic analysis from TG- DTA data.



**Figure 11.** FOX-7 IsoKin – TG-DTA Isothermal Results $T_{iso}$ = 190 - 205 °C.

An isoconversional kinetic analysis was also performed based on the isothermal TG-TGA study with the software *IsoKin*.[11] Figure 11 demonstrates the dependence of activation energy, $E_a$, on the extent of the first step decomposition, $\alpha$. It was noted that the activation energy is constant within the 95 % confidence limits at the initial decomposition step $0<\alpha<0.2$, then decreases gradually in the range of $0.2<\alpha<0.4$, which suggests an autocatalytic reaction. This result agrees well with those obtained from the non-isothermal TG and DSC experiments over the same conversion range.

**CONCLUSIONS**

Cyclic DSC measurements on FOX-7 revealed that the phase changes through the $\gamma$ phase to the $\delta$ phase for the first heating, then reverse to the $\alpha$ phase on cooling, and

transform to δ phase via γ phase on the second heating. The phase reversion from δ to γ on cooling still needs to be further verified due to the its uncertainty and broad feature observed in this DSC measurement, the similar phenomenon has been noticed in the HFC cyclic study in our lab. The equilibrium-inhibited Prout-Tompkins approach has been used for kinetic analysis for these phase transformations.

The total energy released from the two-stage decomposition measured by DSC decreases slightly as heating rate increases, but a more pronounced effect is the substantial decrease in the fraction of heat released in the first peak as heating rate increases. The apparent activation energies obtained via Kissinger's method are 238.3 kJ mol$^{-1}$ for the first decomposition peak and 322.4 kJ mol$^{-1}$ for the second one. Two approaches of isoconversional Friedman-type analysis, and a fit to parallel nucleation-growth reactions have been used for kinetic analysis of the decomposition process. The isoconversional analysis yields an activation energy that is roughly constant for $\alpha > 0.4$. For $\alpha < 0.4$ the isoconversional activation energy varies about the mean value determined from model fitting.

At ambient pressure one exothermic peak is observed in the HFC curve whereas at elevated pressure two exothermic peaks are observed with higher onset temperature of the first peak. This observation suggests that pressure may be one of the factors affecting the decomposition process of FOX-7.

ARC results indicate that a larger sample mass accelerates the self-heating process of FOX-7 and that the time to onset of runaway is decreases as isothermal temperature increases.

The simultaneous TG-DTA-FTIR-MS heating rate study performed in helium and in air shows the evolution of $H_2O$, $CO_2$, HCN, $N_2O$, $NO_2$, and HOCN from the two steps decomposition, and the generation of $HNO_2$ and HCOOH from the second decomposition step. In the second step, more $CO_2$ and HOCN were evolved and a higher mass loss was observed in air than in helium.

The isoconversional kinetic analysis based on the isothermal TG-DTA data shows that the activation energy is approximately constant for $\alpha$ up to about 0.2, then drops gradually as $\alpha$ increases from 0.2 to 0.4, suggestive of a self acceleratory reaction. The results obtained from isothermal experiments are in good agreement with those from the nonisothermal experiments over the same conversion range.

# REFERENCES

[1] H. Bergman, H. Ösmark, M-L. Pettersson, U. Bemm and M. Hihkiö, Some Initial Properties and Thermal Stability of FOX-7, *IM & EM Technology Symposium*, 1999, 346.

[2] I. J. Lochert, FOX-7 - A New Insensitive Explosive, *DSTO*, 2001.

[3] H. Östmark, H. Bergman, U. Bemm, P. Geode, E. Holmgren, M. Johansson, A. Langlet, N.V. Latypov, A. Pettersson, M-L. Pettersson, N. Wingborg, C. Vörde, H. Stenmark, L. Karlsson, M. Hihkiö, 2,2-Dinitro-ethene-1,1-diamine (FOX-7) – Properties, Analysis and Scale-up, *ICT*, 2001, 26-1.

[4] U. Bemm and Lars Eriksson, Phase Transitions in FOX-7, *IM & EM Technology Symposium*, 2001, 775-790.

[5] W. P. C. de Klerk, C. Popescu, A. E. D. M. van der Heijden, "Study on the decomposition kinetics of FOX-7 and HNF, *J. Therm. Anal. Cal.* 2003, 72, 955-966.

[6] D. E. G. Jones, M. C. R. Vachon, R. Wang, Q. S. M. Kwok, Preliminary Studies on the Thermal Properties of FOX-7, *NATAS*, 2004, Williamsburg, VA.

[7] A. K. Burnham, R. K. Weese, B. L. Weeks, A Distributed Activation Energy Model of Thermodynamically Inhibited Nucleation and Growth Reactions and its Application to the $\beta-\delta$ Phase Transition of HMX, *J. Phys. Chem.* 2004, 108, 19432-19441.

[8] J. D. Hoffman and R. L. Miller, Kinetics of crystallization from the melt and chain folding in polyethylene fractions revisited: theory and experiment, *Polymer* 1997, 38, 3151-3212.

[9] B. Roduit, C. Borgeat, U. Ticmanis, M. Kaiser, P. Guillaume, B. Berger, and P. Folly, Thermal stability and safety analysis of explosives under different temperature modes, *35th International Annual Conference of ICT*, 2004, 37-1.

[10] D.E.G. Jones, A.-M. Turcotte and R.C. Fouchard, *Thermochimica Acta*, 2003, 401, 63.

[11] C.A. Wight, "Isoconversional Data Analysis Program", Center of Thermal Analysis, University of Utah, Version 1.42, 2000.