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# High pressure-temperature polymorphism of 1,1-diamino-2,2-dinitroethylene

**M M Bishop[1,2], R S Chellappa[3], Z Liu[4], D N Preston[5], M M Sandstrom[5], D M Dattelbaum[1], Y K Vohra[6] and N Velisavljevic[1]**

[1] Shock & Detonation Physics Group, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[2] Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294, USA
[3] Los Alamos Neutron Science Center, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[4] Geophysical Laboratory, Carnegie Instiution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015-1305, USA
[5] High Explosives Science & Technology Group, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[6] Department of Physics, University of Alabama at Birmingham, Birmingham, AL 35294, USA

Email: nenad@lanl.gov

**Abstract**. 1,1-diamino-2,2-dinitroethylene (FOX-7) is a low sensitivity energetic material with performance comparable to commonly used secondary explosives such as RDX and HMX. At ambient pressure, FOX-7 exhibits complex polymorphism with at least three structurally distinct phases (α, β, and γ). In this study, we have investigated the high pressure-temperature stability of FOX-7 polymorphs using synchrotron mid-infrared (MIR) spectroscopy. At ambient pressure, our MIR spectra and corresponding differential scanning calorimetry (DSC) measurements confirmed the known α → β (~110 ºC) and β → γ (~160 ºC) structural phase transitions; as well as, indicated an additional transition γ → δ (~210 ºC), with the δ phase being stable up to ~251 ºC prior to decomposition. In situ MIR spectra obtained during isobaric heating at 0.9 GPa, revealed a potential α → β transition that could occur as early as 180 ºC, while β → β+δ phase transition shifted to ~300 ºC with suppression of γ phase. Decomposition was observed slightly above 325 ºC at 0.9 GPa.

## 1. Introduction

1,1-diamino-2,2-dinitroethylene ($C_2H_4N_4O_4$), commonly referred to as FOX-7 or DADNE, is among the less sensitive high explosives [1]. While being more sensitive than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), it has comparable performance to related secondary explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [2-4]. Expanding our understanding of high explosives, especially in terms of performance, safety, and development of predictive models, requires a variety of experimental measurements over a broad range of pressure (P) and temperature (T) conditions. Under high-P and/or –T, several of these energetic materials exhibit structural phase transformations and complex decomposition/melt behavior

that can have a direct impact on stability and performance of energetic materials. For example, at ambient-P, FOX-7 undergoes multiple phase transitions with increasing T; $\alpha \rightarrow \beta$ at 111 ± 5 ºC [5-7]; $\beta \rightarrow \gamma$ at 175 ºC [5]; followed by decomposition above 211 ± 7 ºC [7]. Results from differential thermal analysis (DTA) experiments suggest a possible discrepancy in the reported onset of decomposition at ~210 ºC. DTA studies by Chemagina *et al*. [8] suggests that heating FOX-7 slightly above 210 ºC initially leads to an irreversible phase transition to DADNE-T (δ-phase), which can be recovered and was shown to be stable at ambient conditions. Furthermore, it was also shown that a single exothermic peak, associated with onset of decomposition, is only observed in DTA measurements when FOX-7 was heated above ~270 ºC. It is imperative to resolve this discrepancy in the decomposition onset temperature as well as gain insights into the somewhat subtle $\gamma \rightarrow \delta$ transition that extends the thermal stability of FOX-7 by over 60 ºC.

We have been conducting a systematic investigation of the high P-T behavior of FOX-7 to establish the P-T stability of the known high-T (ambient-P) polymorphs as well as explore for new high P-T polymorphs [4]. While, differential scanning calorimetry (DSC) and DTA studies are useful for identifying phase transition (and providing specific heat data), they are typically limited to ambient-P. Using diamond anvil cell (DAC) with *in situ* structural and spectroscopic probes, we recently confirmed earlier reports [9-11] of phase transitions at ~2 GPa and ~5 GPa, at room T [4]. We also conducted some of the first high P-T studies to elucidate the role of hydrogen bonding in the structural stability at these conditions. Based on our ongoing synchrotron XRD measurements, we expect to provide structural details of these high-P phases namely phase I at 2-5 GPa and phase II > 5 GPa. In fact, the most recent work by Dreger *et al*. [12] provides further spectroscopic evidence that the structures of phase I and II are not likely to be similar to known ambient-P, high-T polymorphs. Due to the complexity and challenges associated with high P-T experiments on explosives [13], only a select few HEs have been studied extensively at elevated P-T conditions. Our ongoing studies continue to improve our understanding of the high P-T structural stability, identify new polymorphs, and role of hydrogen bonding network in FOX-7 at P-T conditions leading up to detonation. Recent MIR studies on FOX-7 by Bishop *et al*. [4] have shown evidence for a nearly isobaric phase boundary for phase I and II. Here we present further evidence for the δ-phase suggested by Chemagina *et al*. [8], based on our DSC and DAC synchrotron MIR spectroscopy experiment on FOX-7. In addition, we present a 0.9 GPa isobaric heating MIR spectroscopy experiment tracking the high P-T phase behavior of FOX-7 up to decomposition.

## 2. Experimental Details

DSC measurements were carried out on a TA Instruments model DSC Q2000 with a 0.943 mg sample of FOX-7 in a hermetic aluminum pan. The DSC was run at atmospheric pressure with a 50 ml/min nitrogen flow at a 10 ºC/min heating rate up to 220 ºC. Temperature was then held for 30 minutes at 220 ºC, followed by a decrease at a rate of 10 ºC/min all the way down to room-T. Upon cooling, the sample was held at room-T for 480 minutes, before it was once again heated at a rate of 10 ºC/min up to decomposition.

The high P-T MIR spectroscopy studies were conducted at the U2A beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. For the ambient-P isobaric heating experiment, a sample (~40 μm in diameter x ~10 μm thick) was placed between two type-IIa anvils. However, there was no pressure applied on the sample. The anvils were used to contain the sample during heating up to decomposition temperature. The 0.9 GPa isobaric heating experiment was also preformed using type-IIa diamond anvils and temperature controlled by an internal resistive heater. For high P-T experiments, the sample was placed in a ~150 μm hole, drilled in an Inconel alloy gasket, along with two 20 μm diameter ruby spheres (pressure marker), and KBr (pressure medium). Resulting analysis of MIR vibrational spectra was performed by fitting Gaussians using Peakfit Pro in OriginPro (version 9.0.0).

## 3. Results and Discussion

### *3.1. Differential Scanning Calorimetry*

Results of DSC measurements, consistent with previously reported DTA results [8], indicate that δ-phase is retained at ambient P-T conditions following heat treatment shown in figure 1a. Furthermore, based on DSC data, it also appears that FOX-7 undergoes a partial decomposition, as indicated by change in heat flow measured over a 30 minute period at constant 220 ºC. When compared to a conventional DSC on FOX-7 (1.51 mg with a 10 ºC/min heat rate during a continuous 50 ml/min nitrogen flow up to decomposition), the heat-treated sample indicated no elevated temperature polymorphism and an onset of decomposition starting slightly above 250 ºC (figure 1b).

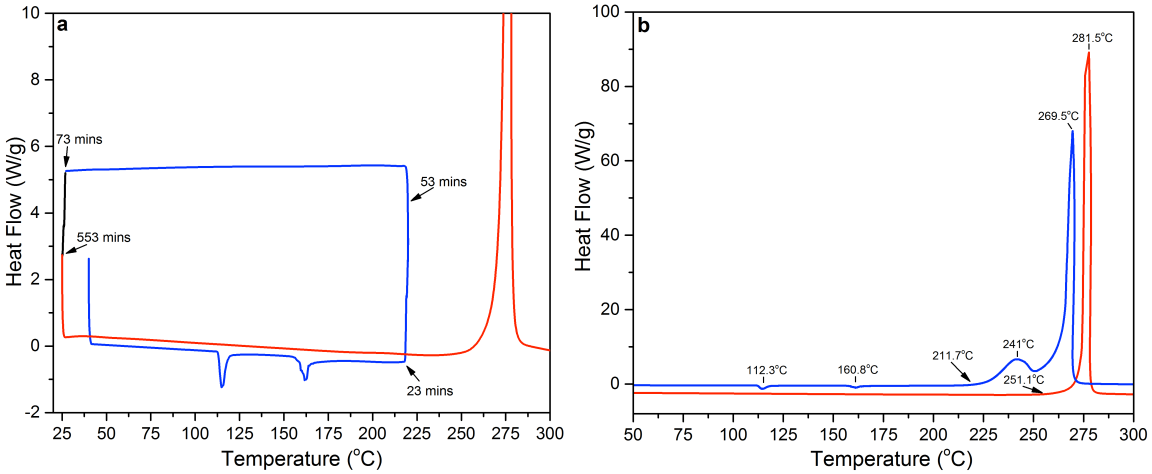


**Figure 1.** (a) The experimental path taken for heat treating FOX-7 as described in the experimental details. (b) A comparison of a normal DSC run (blue, top curve) and heat treated run (red, bottom curve) on FOX-7.

### *3.2. Isobaric Heating (Ambient-Pressure)*

Isobaric heating of FOX-7 at ambient-P indicated a subtle restructuring of the hydrogen bonding network, most notably in the amine stretching modes (3250-3450 $cm^{-1}$), at ~110 ºC (figure 2). The α → β transition has been described as displacive in nature [12] with minor structural distortions that are difficult to resolve spectroscopically (Raman or IR).

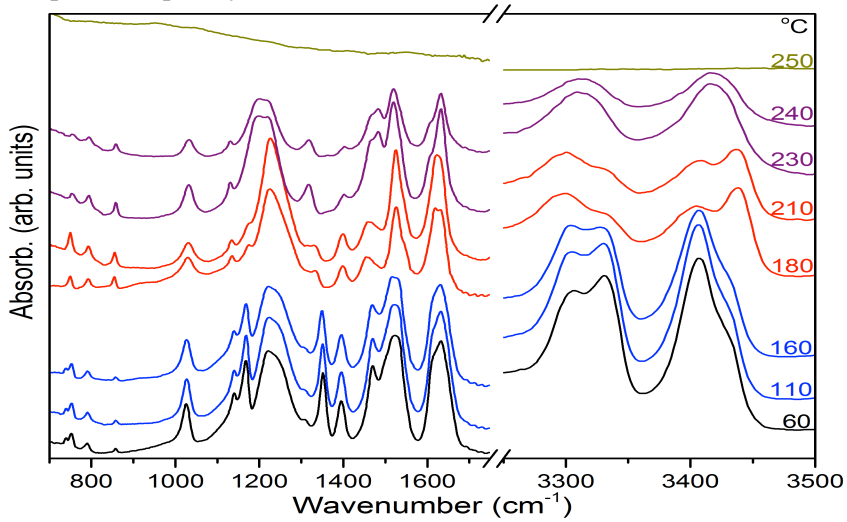


**Figure 2.** Isobaric heating of FOX-7 at ambient pressure up to decomposition. With each high-temperature phase indicated: (α, black; β, blue; γ, red; δ, purple; decomposition, yellow).

With further application of temperature to ~180 ºC, the amine stretching modes (3250-3450 $cm^{-1}$) exhibit several changes including increases in intensities of previously weak features as well as a noticeable shift to higher frequencies. Whereas, the C-$NO_2$ stretching modes at ~1150 and ~1350 $cm^{-1}$ exhibit softening. The β → γ has a clear and very distinct infrared signature; which was expected due to the highly energetic behavior detected by DSC (figure 1a,b). Based on our DSC results, we also expected that γ → δ should have a very unique infrared signature: however, the actual time scale of partial decomposition and transitioning into the δ-phase points to a highly kinetically driven effect. Indeed, only upon reaching 230 ºC do we observe the unique infrared signature of the δ-phase. Most notably the amine stretching modes (3250-3450 $cm^{-1}$) are now softened by ~10-20 $cm^{-1}$; as well as being accompanied by the loss of vibrational modes at ~1526, 1335, and 1180 $cm^{-1}$. The observed softening and disappearance of some modes indicates that the partial decomposition (as shown as the exotherm starting at ~211 ºC in (figure 1b) obviously has a large effect on the molecular crystal structure. Furthermore, due to possible kinetic affects, there may be a mixture of γ-δ phases over a broad T range. It should be noted that coexistence of γ-δ may also explain difficulty in resolving x-ray diffraction data and limited high-T structural information available on FOX-7. Upon further heating, decomposition is observed starting at ~250 ºC. Comparison between our ambient-P high-T MIR measurements and our DSC data helps us determine the infrared signatures for each phase of FOX-7; information that can then be applied for further high P-T experiments on FOX-7.

*3.3. Isobaric Heating (0.9 GPa)*

Isobaric heating at 0.9 GPa indicates an onset of α → β occurring as early as 180 ºC, but is most 'defined' at 220 ºC: as indicated by a subtle restructuring of the hydrogen bonding network, marked by alterations to the amine stretching modes (~3250-3450 $cm^{-1}$). It is important to note that based on the collected MIR spectra, it is difficult to clearly identify onset of α and β transition. A further, more robust, investigation of the α to β transition will be required to clearly establish the high P-T phase boundary.

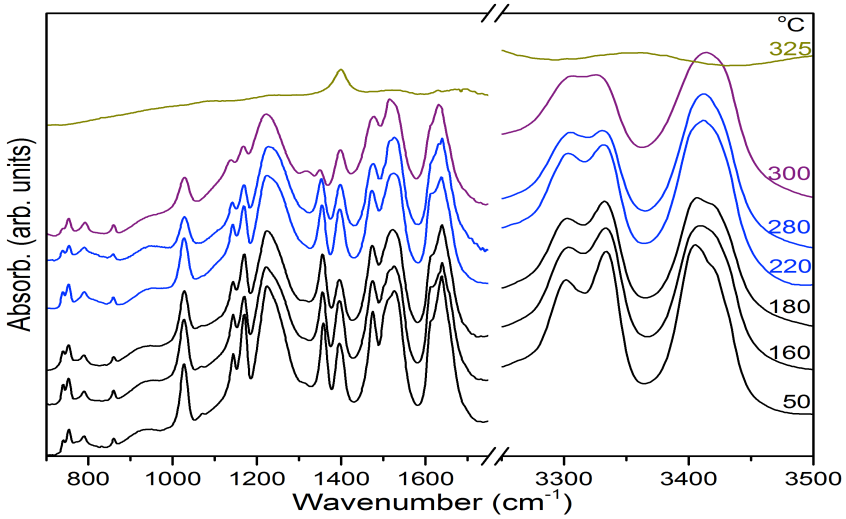


**Figure 3.** Isobaric heating of FOX-7 at 0.9 GPa up to decomposition. With each high-PT phase indicated by the following schema: (α, black; β, blue; β+δ, purple; decomposition, yellow).

Based on preliminary data analysis, the α → β phase boundary appears to have a steep ~70-90 ºC/GPa slope. Upon further heating, a mixed phase of β+δ occurs at ~300 ºC: as indicated by the alterations to the amine stretching modes (~3250-3450 $cm^{-1}$) and C-$NO_2$ stretching mode near 1350 $cm^{-1}$ (figure 3). Analysis of the 0.9 GPa 300 ºC MIR spectrum was conducted by overlaying this spectrum with a β, γ, and δ MID spectra collected in the ambient-P high-T experiment. From the analysis of high-P spectra

versus spectra collected at ambient-P, we conclude that elevated-P spectra contains signatures of both β+δ mixed phase. We suspect, as discussed earlier, kinetics effects may be playing a significant role in resolving the δ-phase, which may not have fully completed on time scale of our measurement. The experiment was completed with further heating and decomposition of FOX-7 at ~325 ºC, which indicates a very steep (~75 ºC/GPa) increase in solid-decomposition boundary with pressure.

## 4. Conclusion

Emergent work published continues to point to a very complex behavior of energetic materials at high P-T conditions [1-13]. Resolving multiple solid-solid transitions and determining onsets of decomposition is crucial to further improve our understanding of the behavior of energetic materials. We have used a combination of DSC and MIR measurements to provide a glimpse into structural stability and decomposition of FOX-7 at elevated pressures. Initial room-P high-T measurements were used to establish comparisons between changes measured in DSC to those observed in MIR DAC experiments. Based on initial DSC and MIR data, we were able to identify key features in IR spectra marking onsets of various solid-solid transitions and decomposition boundary. This information was then used to further help in resolving high P-T behavior of FOX-7.

Our DSC MIR measurements confirm the previously reported α → β → γ transition in FOX-7 at room-P and high-T. Furthermore, we also observe evidence for δ phase and decomposition above 250 ºC [8]. Heating at 0.9 GPa is again marked initially by a number of solid-solid transitions (α → β → δ), followed by decomposition above 300 ºC. During isobaric heating at 0.9 GPa, we do not observe clear evidence of γ phase, suggesting that this phase may be terminating at lower pressure. Additional experiments are needed, and are in progress, in order to further resolve the complex behavior of FOX-7 at high P-T.

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