HiPSEC X-Ray Diffraction and Infrared Spectroscopy Studies on Energetic Materials under Extreme Conditions

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Abstract

We conducted a series of experiments on the decompositions of the energetic materials $NaBH_4$, NH_3BH_3, HMX, and RDX under different pressures using the x-ray diffraction (XRD) technique; we also studied the lesser known but high-performance explosive FOX-7's behaviors under high pressures using the infrared spectroscopy (IR) technique. For the chemical decomposition of $NaBH_4$ and NH_3BH_3 we discovered possible x-ray induced hydrogen gas generation; for the decomposition of HMX and RDX, we discovered that the decay rates of these two materials vary with pressure respectively; for the study of FOX-7's high pressure behaviors we discovered potential phase changes and pressure induced chemical reactions as pressure is increased.

X-Ray Induced Chemistry in Hydrogen Rich Materials: $NaBH_4$ and NH_3BH_3

❑ **Materials Description**

$NaBH_4$ (sodium borohydride) and NH_3BH_3 (ammonia borane) are potential hydrogen storage materials that are currently subjected to intensive research. Under the proper conditions, these materials can release hydrogen gas (2 molar equivalent for $NaBH_4$ and 6 for NH_3BH_3). The current researches focus on heat or catalyst induced hydrogen generations, which proved to be too uncontrollable to be used in applications.

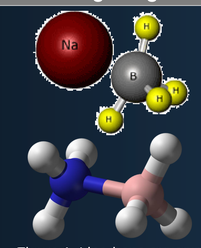

Figure 1. Line-bone structures of $NaBH_4$ and NH_3BH_3 respectively

❑ **Experiment**

We mixed the $NaBH_4$ powder and NH_3BH_3 powder with $KClO_3$ (potassium chlorate) powder respectively. $KClO_3$ acts as a detector in this experiment. Under x-ray bombardment, the hydrogen gas is released from the hydrogen rich compounds and reacts with the oxygen gas generated from $KClO_3$ and form liquid water. We will be able to detect the existence of water both visually and through spectroscopy and confirm the release of hydrogen gas.

❑ **Results and Discussions**

There are several indications of chemical reactions in both mixtures. In fig. 2, the relative intensities of the peaks in the XRD spectra of the $NaBH_4$+$KClO_3$ changed as the x-ray bombardment proceeded; in fig. 3, as indicated by the XRD spectra, the $KClO_3$ in the mixture is decomposed by the x-ray into KCl; and in fig. 4, we can observe the formation of water from the reaction in the NH_3BH_3 + $KClO_3$ mixture visually, indicating the possibility of hydrogen release from NH_3BH_3.

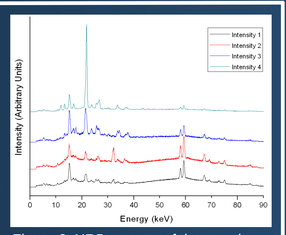

Figure 2. XRD spectra of the reaction mixture ($NaBH_4$+$KClO_3$) stacked in chronological order from bottom to top.

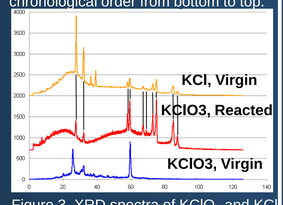

Figure 3. XRD spectra of $KClO_3$ and KCl

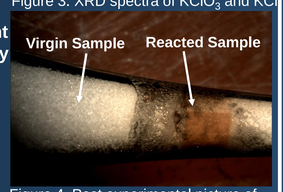

Figure 4. Post experimental picture of NH_3BH_3+$KClO_3$ mixture. The liquid bubbles are water formed in the reaction.

High Pressure Study of FOX-7 Using Infrared Spectroscopy (FOX-7: 1,1-diamino-2,2-dinitroethene)

❑ **Material Description**

FOX-7 is an insensitive high power explosive compound. it has a two-carbon backbone, and the amino and nitro groups contribute to sensitivity and chemical decay processes of FOX-7, similar to most other nitrogen-containing explosives.

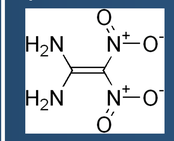

Figure 1: skeletal structure of FOX-7

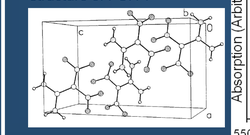

Figure 2: FOX-7 crystal

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❑ **Experiment**

At Brookhaven National Laboratory, a small amount of FOX-7 crystal was loaded in a diamond anvil cell (DAC) and placed under infrared (IR) laser. Spectra were taken under several different pressures.

❑ **Results and Discussions**

In fig. 3 the major functional groups are labeled under their corresponding peaks (tetra-substituted CC double bond does not have IR absorption). In fig. 4 we can observe, according to the peak intensities, that the NH_2 and NO_2 asymmetrical stretch are diminishing as pressure increases. The peak around 1100 cm^{-1}, which we believe to be the amine C-N stretch, increases in intensity as pressure increases. These are indications of possible phase changes and pressure induced chemical reactions.

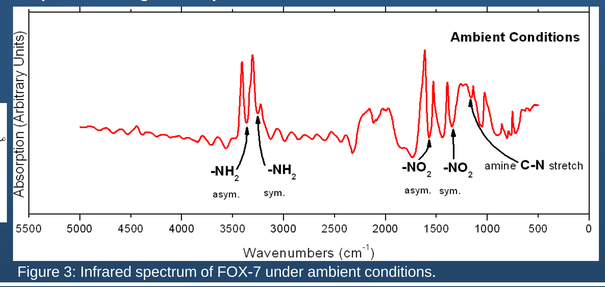


Figure 3: Infrared spectrum of FOX-7 under ambient conditions.

Figure 5: FOX-7 crystal before and after x-ray bombardment respectively. (X-ray used is synchrotron x-ray from the Argonne National Laboratory's Advanced Photon Source).

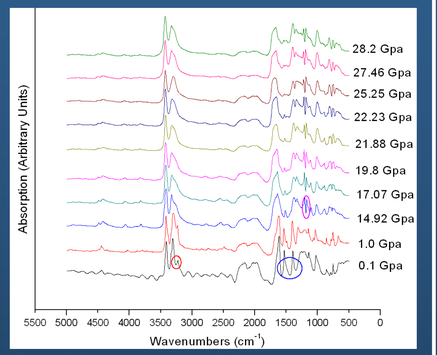
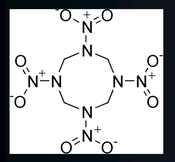
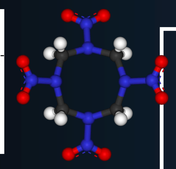


Figure 4: Stack graph of FOX-7 IR spectra in order of increasing pressure. Peaks of interest are circled.

High Pressure Study of X-Ray-Induced Decay of HMX Using XRD (HMX: Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)





❑ **Material Description**

HMX, also called octogen, is a powerful and relatively insensitive high explosive. It is a high melting, high-velocity military explosive.

The molecule of HMX is an eight-membered ring of alternating carbon and nitrogen atoms. Because of its high molecular weight, it is one of the most potent chemical explosives manufactured.

❑ **Experiment**

We placed HMX powder in a Paris-Edinburgh cell and subjected it to x-ray bombardment under three different pressures (0.65 GPa, 3.2 GPa, and 5.65 GPa). We took x-ray diffraction (XRD) spectra of the sample over the course of the bombardments to monitor the decay of the sample. (fig. 1)

❑ **Results and Discussions:**

We selected two most prominent peaks from the XRD spectra and plotted their intensities as functions of time. We integrated the decay curves for three different pressure points (fig. 2). The integrated decay curve shows that the decay rate of HMX under x-ray bombardment slows down as pressure increases. The reason of this effect would be the focus of our follow-up studies.

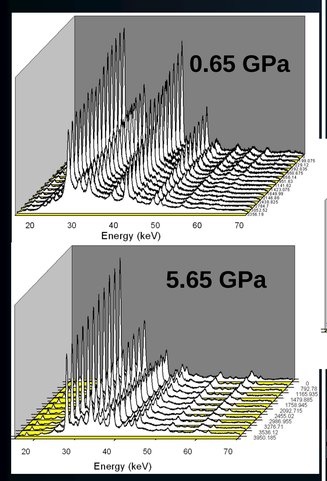


Figure 1. Integrated XRD spectra of HMX with respect to time. The pressures under which the sample was bombarded are labeled on the pictures.

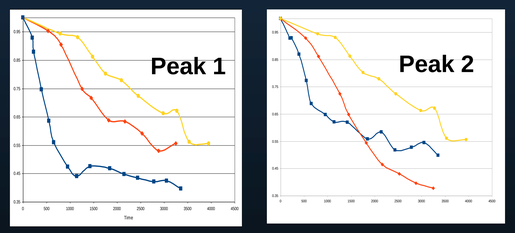


Figure 2. Integrated decay curve of HMX. The peak intensities are selected from two peaks and are plotted with respect to time. The blue, red, and yellow lines indicate decays at 0.65, 3.2, and 5.65 GPa respectively.

High Pressure Study of X-Ray-Induced Decay of RDX Using XRD (RDX: 1,3,5-Trinitro-1,3,5-triazacyclohexane)

❑ **Material Description**

RDX is an abbreviation for Research Department Explosive. It is an explosive widely used in military and industrial applications.

It is stable in storage and is considered one of the most brisant of the military high explosives.

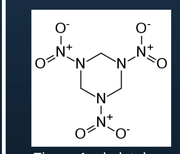


Figure 1: skeletal structure of RDX

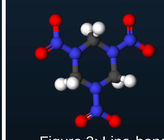


Figure 2: Line-bond structure of RDX

❑ **Experiment**

We placed HMX powder in a Paris-Edinburgh cell and subjected it to x-ray bombardment under different pressures and temperatures. We took XRD spectra of the sample over the course of the reaction to monitor the decay of the sample. (fig. 4)

❑ **Results and Discussions**

The decay rate of RDX under x-ray bombardment increases sharply as pressure increases and then decreases slowly as pressure increases further (fig. 3). This is an indication of possible phase transitions.

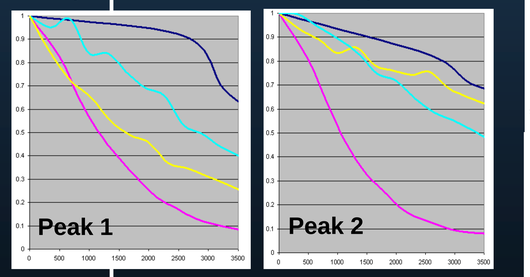


Figure 3: Integrated decay curves of RDX decay under x-ray for two separate peaks. The blue, pink, yellow, and cyan lines indicate decay curves for 0, 2.5, 4.15, and 5.26 GPa respectively.

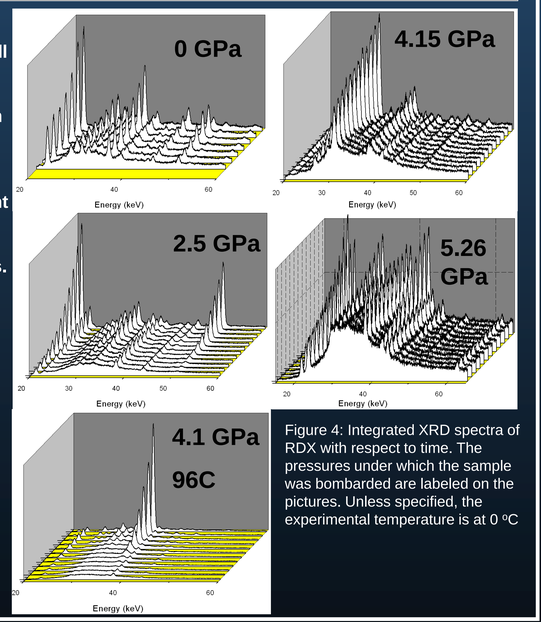


Figure 4: Integrated XRD spectra of RDX with respect to time. The pressures under which the sample was bombarded are labeled on the pictures. Unless specified, the experimental temperature is at 0 °C

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