ANALYSIS OF HIGH ENERGY DENSITY MATERIALS USING DENSITY FUNCTIONAL THEORY AND MOLECULAR MODELING

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Abstract

High Energy Density Materials are difficult to analyze experimentally, and little is known about their decomposition mechanisms. Computational chemistry techniques, such as DFT and molecular modeling allow for the trigger bonds and sensitivities to be predicted. Wiberg bond index was used to determine trends between the bond strength and impact sensitivity for a series of nitro and nitramine compounds. %WBI gives a good prediction of the trigger bond but is not as liked to the impact sensitivity, most likely due to being calculated in the gas phase, where the impact sensitivity is obtained in the solid phase. Oxygen balance does not relate to the bond strength of the molecule but does slightly correlate with the impact sensitivity due to increasing the oxygen balance through the addition of more nitro groups. Stronger predictions for the decomposition mechanism can be obtained using molecular modeling which runs calculations in the solid phase. Quantum Espresso simulations are being analyzed for the species production during the reaction to determine the decomposition mechanisms at different pressures.

Introduction

On November 16, 2022, NASA launched the Orion spacecraft and Space Launch System (SLS) for the Artemis I mission, the first of many steps for traveling to the moon and to Mars. Orion flew around the moon and returned to Earth on December 11, 2022.[1] The SLS produced 8.8 million pounds of thrust during take-off through twin boosters that use a solid propellant called ammonium perchlorate composite propellant (APCP).[2] APCP was developed in 1954 and given enough surface area inside the fuel tanks, will burn evenly, reducing the risks of explosions.[3,4] The R-25 engines that propel the Orion spacecraft employ the reaction of liquid hydrogen and liquid oxygen to move the craft through space.[5] Previously, hydrazine was the fuel of choice. However, this was a factor that caused the Columbia disaster in 2003 and made the cleanup difficult. Explosions at Wallops Island and the Kennedy Space Center in 2014 and 2015 were detrimental to the surrounding environment due to contamination from the fuels on board.[6] APCP and liquid hydrogen and oxygen are safer for the environment and for the workers who load them on the rockets, but still pose risks and are not very energy efficient. APCP produces hydrochloric acid when the byproducts are mixed with water, and the hydrogen and oxygen must be cooled to extremely low temperatures to maintain their liquid forms.

Propellants are part of a class of compounds known as High Energy Density Materials (HEDMs), including explosives. These materials are used for mining and military operations, pyrotechnics, and space flight.[7,8] Commonly used HEDMs include trinitrotoluene (TNT), hexahydro-1,3,5-triazine (RDX), and nitroglycerin all contain nitro functional groups which are thought to be explosophores or the groups that break off and initiate the cascade of reactions that make up an explosion. Other explosophores are nitramines, nitric esters, azo groups, and nitriles. These are found on the trigger bond or the bond that first breaks to start the decomposition.[7] Understanding the decomposition mechanisms of HEDMs is important to understanding why certain compounds are so effective as HEDMs and why others are not. New HEDMs that have a higher energy density can be developed, are less sensitive to stimuli, and do not release harmful gases as they break down.[8] These new fuels and explosives will help get space

exploration to further planets and make mining to collect samples easier and less likely to contaminate the materials.

Impact, shock, and friction can all affect HEDMs in different ways, and gaining an indication of how sensitive a compound is to each one is crucial to being able to use them safely.[9–11] Impact is the most measured through a drop hammer test. A portion of the compound is placed on an anvil and either a 2.5kg or 5kg weight is dropped onto it from a predetermined height. A series of drops is performed from each height and the height at which the compound explodes during half of the runs is the h50 recorded in centimeters. This provides an idea of how sensitive the compound is and if it is viable to work with in the future.[9–11]

HEDMs react violently and produce a lot of heat and gases. Due to this nature, studying them experimentally is a challenge as they could easily destroy instrumentation or harm the researchers working with them.[8,12–14] Computational methods, such as density functional theory (DFT) and molecular modeling (MM) provide a safer and more cost-effective way to study the compounds.[15] Studies give insight on the quantum properties of the molecules allowing for the prediction of the trigger bonds and decomposition mechanisms. The Wiberg Bond Index (WBI) is a measure of electron density in a bond and has been used to identify the trigger bond in traditional and novel HEDMs.[16] The WBI, or the sum of the off-diagonal square of the density matrix D is calculated through equation 1.

$$WBI_{AB} = \sum_{p\epsilon A}\sum_{p\in B}(D_{pq})^2 \qquad (1)$$

The one-step calculation required to obtain WBIs reduces the error in modeling intact fragments that other methods, such as bond dissociation energy, can add to the results. On its own, WBI is not adequate to predict the bond strength, but when compared to a reference molecule that contains the same bond type, hybridization, and atom linkage, a relative scale of electron density can be obtained and used to identify the trigger bond, or the %WBI (equation 2).[17–20]

$$\%WBI_{AB} = \frac{WBI_{AB}(HEDM) - WBI_{AB}(reference)}{WBI_{AB}(reference)} \qquad (2)$$

Negative %WBI values demonstrate an activated bond because of the decreased electron density. The bonds with the lowest %WBI in the molecule are more likely to break under stress.

Oxygen balance (OB) is a predictor of product formation during decomposition using the chemical formula and molecular weight of the molecule (equation 3).[7,21]

$$\Omega = \frac{\left[d - 2a - \frac{b}{2}\right] \times 100}{M} \qquad (3)$$

When the OB is less than zero, there is not enough oxygen present to completely oxidize the hydrocarbon backbone of the material. Toxic gases, such as CO and NO_x, are formed, creating harmful conditions for the environment and the user.[7]

DFT calculations are computationally cheap and can provide quick approximations on the quantum properties of individual molecules of a substance in the gas phase.[9,11,22–24] A few drawbacks occur in these simulations with compromising time. The main factor that is missed when doing gas phase calculations is the intermolecular interactions that occur when the compounds are in the solid or liquid phase. Most HEDMs are used either in the solid or liquid phase, and the experimental testing of sensitivity to shock, friction, and impact is all done in the solid state. Discrepancies occur in the prediction of the trigger bond and decomposition often due to missing the interactions of the molecules around it that could either stabilize or destabilize a bond that appears to be weaker. Molecular Modeling (MM) and Molecular dynamics (MD) simulations are run in the solid state from the

crystal structures of compounds and includes intermolecular interactions.[9,11,22–24] During this study, both DFT and MM simulations were run on HEDMs to further the understanding of their decomposition mechanisms and sensitivity to stimuli.

Methods

DFT Study

The optimization of 143 different HEDMs was done in the gas phase using Gaussian09[25] and the hybrid M06-2X[26] functional and triple-ζ basis set augmented with polar functions (TZVP).[27] TZVP was selected due to the basis set dependence that WBI calculations have when diffuse functions are included which was noted in our previous work.[17] WBI calculations were done on the optimized structures through NBO analysis Version 3.1.[28] The dataset of molecules was selected from two papers that included the experimental h_{50} information that was obtained from only two labs, eliminating some variables from obtaining the data. The dataset contains molecules with nitro, nitramine, nitric ester, and azo explosophore groups.[29,30]

MM Study

The crystal structures of RDX, ammonium nitrate, TATB, and 1,1'-azobis(tetrazole) have been optimized using Quantum Espresso 6.1.[31,32] Optimization simulations were run on each unit cell with a 1x1x1 k-point grid. Ultrasoft pseudopotentials were used with the Rappe Rabe Kaxira Joannopoulos method and Perdew-Burke-Ernzerhof (PBE) exch-corr scalar relativistic functional. Then decomposition simulations were run at constant temperatures but varied pressures. To analyze the results, DeepMD and ReacNetGenerator in combination with Matlab determined the species at each time step.[33]

Results and Discussion

DFT Study

143 HEDMs were DFT(M06-2x/TZVP) optimized and were consistent with available DFT calculations and crystal structures. The set was chosen to determine whether %WBI and oxygen balance could predict impact sensitivity. The molecules contain the aliphatic nitros, aromatic nitros, and/or nitramines, which based on previous studies, are predicted to be the trigger bond for the compounds.

For each of the trigger bond types, the bond length strongly correlated with the %WBI (Figure 1). %WBI demonstrates the change in electron overlap between two bonded atoms from the reference molecule. A negative %WBI indicates a loss of electron density and therefore a weakening of the bond. As two atoms are pulled farther apart, the electron density decreases. When the bond length is shorter, the %WBI is more positive, demonstrating a stronger bond, which can be seen in all trigger bond types (Figure 1).

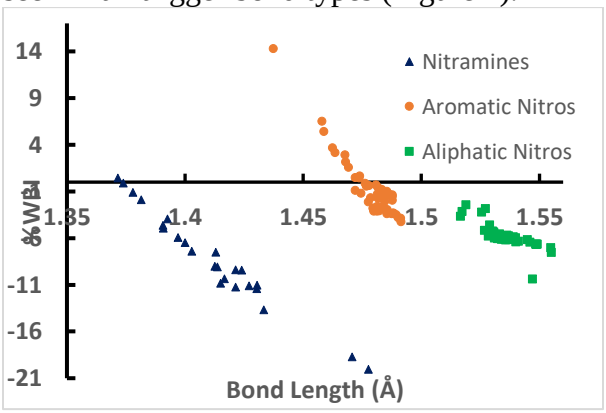

Figure 1. The bond activation increases as the bond length increases as demonstrated by the increasingly negative %WBI values.

Impact sensitivity is commonly used to determine if a HEDM can be used safely and still provide the desired result. A drop hammer test was done on all 143 compounds by two laboratories to give the h_{50} number, with a higher value demonstrating a less sensitive compound. When the %WBI was plotted

against the h_{50} values for each compound, there was no correlation. Then the %WBI and h_{50} values for aliphatic nitros, aromatic nitros, and nitramines were plotted separately (Figure 2).

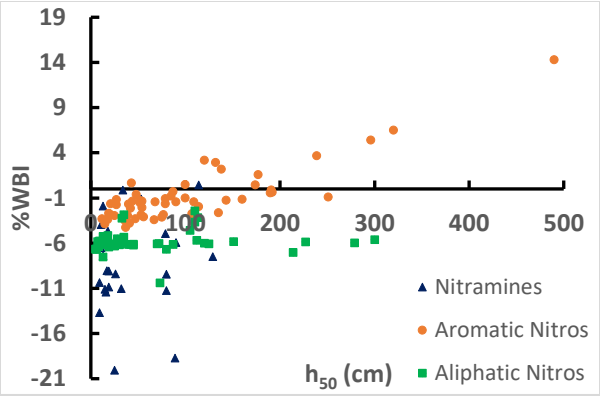

Figure 2. Bond activation and impact sensitivity are loosely linked for aromatic nitro compounds but do not show a correlation for nitramines and aliphatic nitros.

For nitramines, there was a correlation between the values, and for aliphatic nitros, there is a slight trend, but the line also contains many outliers. Aromatic nitros, however, had a loose correlation with an R^2 factor of 0.7219 (Figure 3).

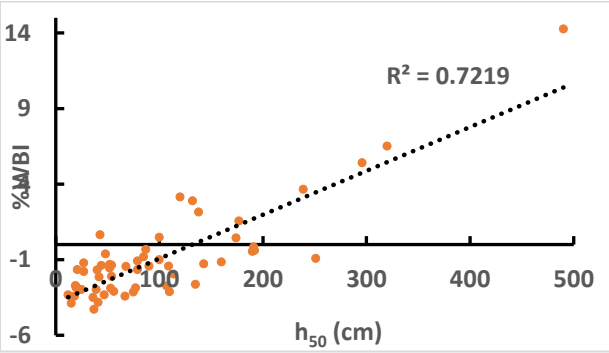

Figure 3. A correlation between the bond strength and impact sensitivities demonstrates that weaker bonds can predict sensitivity.

The trend indicates that as the bond becomes weaker and more activated, it becomes easier to break and requires less force from impact that start the decomposition. The lack of trends with both the aliphatic and nitramine groups is likely due to the calculations being completed in the gas phase. Most of these molecules in the dataset are longer chains and have many different conformations, with only a few of them having the crystal structure solved. The lowest energy conformation in the gas phase, may not be the conformation that the molecule takes on in the crystal, which could lead to intramolecular interactions that would lead to a change in the strength of that bond. Intermolecular interactions in the crystal structure could also affect the strength of the trigger bond, but those are not factored in with this calculation. Obtaining an accurate h_{50} value is also difficult. Variables such as how the compound was crystallized, the laboratory environment, the experimentalist, the composition of the hammer and anvil, and how an explosion is recorded can all alter how the compound responds to stimuli and would affect trends.

OB has previously been used to predict impact sensitivities, with OB greater than zero having enough or more than enough oxygen to completely oxidize the hydrocarbon backbone of the structures, and theoretically making it easier for the compound to undergo the full decomposition mechanism. When the OB was plotted against the experimental h_{50} values, a slight logarithmic trend can be seen for each bond type (Figure 4).

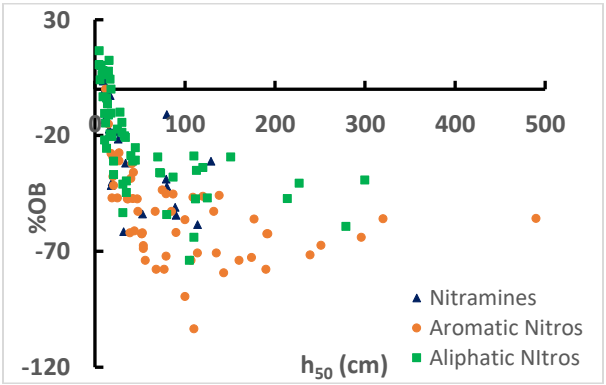

Figure 4. OB has a loose correlation to impact sensitivity for each of the bond types.

The more positive the oxygen balance becomes, the lower the h_{50}, indicating that the sensitivity is increasing. When plotted against %WBI, there is no trend between the bond strength of the trigger bond and the OB (Figure 5). OB can predict the products that will be produced during decomposition but cannot give an indication of the electronic properties of the molecule.

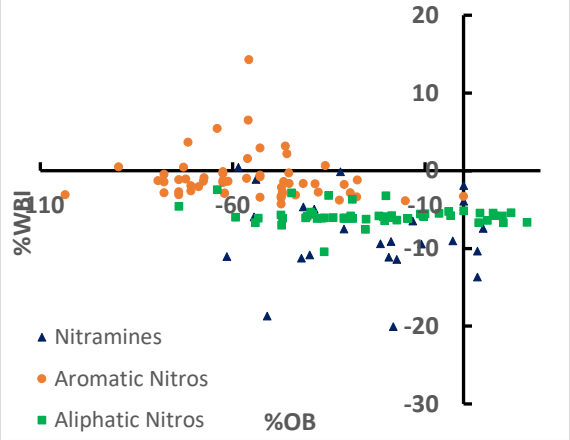

Figure 5. The OB does not have any correlation to that of bond strength, as seen when plotting them against each other.

Oxygen balance is commonly increased through the addition of more nitro functional groups around the molecule, and all of them are explosophores. The more explosophores a molecule has, the more likely one of them is to break off when energy is applied to the compound, which could explain the trend in Figure 4. When a nitro group is added to a molecule, the OB increases, but the %WBI does not always decrease, indicating that OB is not linked to bond sensitivity (Figure 5).

MM Study

Single-molecule calculations with DFT do not consider electrostatic interactions that can occur while in the crystal structures. Molecular modeling simulations use the unit cells from X-ray crystallography so that those factors can be applied to the calculations. Quantum Espresso is a molecular modeling simulation that uses plane wave-DFT (PW-DFT) to simulate the molecules over a period. Unit cells of RDX, TATB, acetyl nitrile, and 1,1-azobis(tetrazole) were set up and relaxed at 1atm. Then the simulations were put under various pressures to see how the decomposition mechanisms would respond (Figure 6).

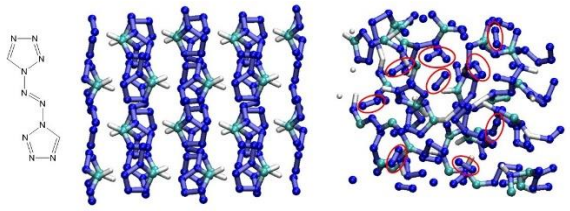

Figure 6. A 1,1'-azobis(tetrazole) unit cell at ambient pressure and 0 ps (left) compared to the unit cell at 10 ps into the simulation at 275 Katm. The red ovals indicate N_2 formation as the simulation progresses demonstrating that the azo bridge is the trigger bond.

These simulations contain thousands of frames, and each frame has hundreds of atoms and species, making analyzing the results challenging. To count the species and be able to monitor the reactions, a program called ReacNetGenerator was used along with another, DeepMD, which trained the algorithm for classifying bonding and atom types. Using these programs, species formation can be tracked, and the trigger bond and decomposition mechanism can be determined (Figure 7).

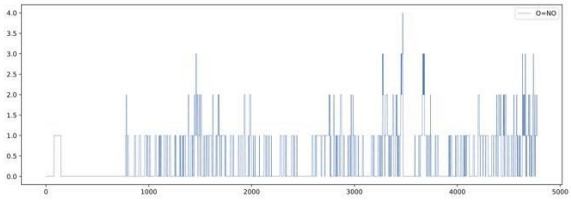

Figure 7. A plot of the number of O=N-O species that was formed during a simulation of RDX at 1atm in Quantum Espresso.

Conclusion

Traditional HEDMs have been difficult to study experimentally due to their violent reactions, but DFT and MM give insight into their decomposition mechanisms and sensitivities. %WBI is a valuable tool to identify the trigger bond but is limited in determining the impact sensitivity due to being a single-molecule method, while h_{50} is obtained in the solid state. OB appears to have a correlation to impact sensitivity, but it only looks at the physical makeup of the molecule and does not include the electronic properties. The link is most likely due to increasing the oxygen balance by increasing the number of nitro groups, which is adding more explosophores to the molecule, increasing the chance that the molecule will explode. MM provides the electrostatic interactions found in the solid-state and can give a better estimate of the trigger bond and the decomposition mechanism. Further simulations and analysis of those simulations needs to be done on the molecules to determine the affect of pressure on the mechanisms.

Acknowledgements

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