ANALYSIS OF THE DECOMPOSITION MECHANISMS OF HIGH ENERGY DENSITY MATERIALS USING DENSITY FUNCTIONAL THEORY AND MOLECULAR DYNAMICS SIMULATIONS

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Abstract

Experimental analysis of high energy density materials (HEDMs) is difficult and dangerous because they are sensitive to explosive decomposition. However, the military, aerospace industries, and mining companies are interested in developing cleaner HEDMs with a higher balance of stability and strength. DFT and molecular modeling have been used to predict the decomposition mechanisms and identify properties that affect sensitivity without putting the experimentalist and instrumentation at risk. Computational approaches such as oxygen balance, HOMO-LUMO gaps, and bond strengths have been used to correlate to the impact sensitivity to varying success. Our group has focused on the use of Wiberg Bond Indices to identify the bonds that trigger detonation. However, these simple calculations are limited because they lack information about solid-state intermolecular interactions. This talk reviews these methods for a large dataset of HEDMs and demonstrates a need for condensed phase simulations of the detonation process and properties affecting the impact sensitivity.

Introduction

High Energy Density Materials (HEDMs) are compounds that contain a high amount of potential energy and release that energy instantaneously through the expansion of gases.[1–4] These reactions can be controlled (propellants) or not (explosives) and used in mining operations, military activities, pyrotechnics, and space flight.[1,2] Conventional explosives, such as 2,4,6-trinitrotoluene (TNT) or 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), consist of a carbon backbone with explosophore substitutions.[1,3,4] Explosophores are functional groups that increase the potential energy of the molecule, which include aromatic and aliphatic nitros, nitramines, nitric esters, azos, and azides.[1,5] These compounds typically have insufficient oxygen to fully combust into water and carbon dioxide, which allows for the formation of toxic NO_x and CO_x gases.[1,5]

The first explosive developed was black powder in 220 BC by Chinese alchemists but did not become commonly used until the 13th century as an aid to breach castle walls and later in guns and grenades.[1] In the late 1800s and early 1900s, nitroglycerin, nitrocellulose, and dynamite were developed to produce a more powerful and safer compound for mining.[1] The manufacturing of these explosives was done close to the mines to try and reduce the number of casualties caused by accidental detonations.[1] Modern HEDMs, such as RDX, HMX, and hydrazine, are more stable and typically only react when purposefully detonated.[1,3,4] However, these compounds produce toxic byproducts from their use which can harm the people using them and the environment. Hydrazine is a common rocket fuel, is toxic to all living things, and poses a great threat to the environment during launches.[6] Cleaning up any failed launches, like the Wallops Island or the Columbia disasters, becomes more difficult from the contamination.[6] Due to these problems, new HEDMs need to be developed to balance the

sensitivity and power of the compound and reduce the harmful byproducts from use.

To improve traditional HEDMs, understanding the decomposition mechanism for the compounds is necessary. Current thinking is that HEDMs break down through HONO elimination, X-ONO rearrangement, or a homolytic cleavage at the explosophore with the last being thought of as the favored mechanism.[7–14] Studying these reactions experimentally is challenging due to the instantaneous and violent way they react. In some cases, an HEDM is analyzed by FTIR or MS at increasing temperatures to see what functional groups change, however, this does not account for the extremely elevated temperatures and pressures that occur during an explosion.[10–16]

Another property necessary to understand is the sensitivity to impact, friction, shock, and temperature. HEDMs respond differently depending on what they encounter, but the most studied is impact sensitivity.[1] A drop hammer test is used to obtain a measurement of the sensitivity, where a 2.5 or 5 kg weight is dropped on a sample at predetermined heights in a series. Using microphones or cameras to detect light, the experimentalist determines if an explosion occurred. When the compound explodes fifty percent of the series, that is the h50, is reported in centimeters.[17–19] However, many variables can affect the results: the laboratory environment, the composition of the hammer and anvil, the crystallization of the sample, and the experimentalist.[17–19] This makes obtaining an accurate measurement difficult and puts the experimentalists at risk.

The challenges that occur with testing these materials experimentally lead to computational chemistry being an essential tool for gaining new insight into them. They save money by reducing lab time and materials used and reducing the risk of injury. The computational methods can be grouped into two major categories: single-molecule gas-phase and solid-state molecular dynamics, both of which are used to try and determine the trigger bond and predict properties of the compounds.[20,21] A trigger bond is a bond that breaks and initiates the chain reaction of the explosion, which gives insight into the mechanism of decomposition.[1,22–24] Using the trigger bond and mechanisms of traditional HEDMs, trends are identified to give a prediction of the sensitivity and power of the material.

A common single-molecule calculation is oxygen balance, which uses only the molecule's chemical formula.[1,22] Oxygen balance, calculated by the formula:

$$OB = \frac{\left(d - 2a - \frac{b}{2}\right) * 100}{M} \quad (1)$$

Where a is the number of carbons, b is the number of hydrogens, c is the number of nitrogens, d is the number of oxygens, and M is the molecular mass, providing an insight into what products will be formed during the reaction. If OB is less than zero, there is not enough oxygen present in the molecule to completely oxidize the carbon backbone, and toxic gases will be created.[1] Researchers such as Kamlet have attempted to correlate OB to h50 to predict new compounds' sensitivity, however, this only gives a loose correlation with compounds that have the same class of explosophore.[22] This calculation leaves out electronic properties or steric effects in the molecule which could cause stabilization or destabilization.

The difference in energies between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) has been studied to correlate with impact sensitivity.[19,25] When a HEDM encounters an impact, energy is sent

through the molecule which can excite electrons into higher energy orbitals resulting in bonds breaking or forming. The closer the HOMO-LUMO gap is, the less energy is needed to cause a reaction. Theoretically, this should show that a smaller HOMO-LUMO gap correlates to a more sensitive molecule, but studies have shown that this is not the case. The contribution from surrounding molecules plays a larger role in the sensitivity than this energy gap.[19,25]

Electron density is used to identify a molecule's trigger bonds either by using the Quantum Theory of Atoms in Molecules (QTAIM) method or by using electrostatic potentials (ESPs).[19,26–28] In QTAIM, the electron density is calculated using the wave function and then plotted on a topographical map. Critical points are identified using the curvature of the density and can show where there is less overlap between two atoms in a bond. The less overlap seen indicates a weaker bond, which likely will be the trigger bond.[19,26] ESPs also use electron density by considering each atom's charges individually and then projecting that across the entire molecule.[19,27,28] Because the ESPs look at individual atoms, bond strength can be determined in two ways, either by looking at the electrostatic potential at the midpoint of the bond, with the more positive being a weaker bond, or by looking at the different in the potential between the two atoms, with the smaller difference being weaker.[19,27,28] In both the QTAIM and ESP studies, some correlation between impact sensitivity and electron density has been found.[19,27,28] Still, these only work for small subsets of HEDMs and must have the same explosophore types, which does not help with analyzing novel compounds.

Bond dissociation energy (BDE) is another technique used to determine the trigger bond.[19,29,30] The calculation looks at the enthalpy change that occurs during bond breaking and the higher the BDE, the more difficult that bond is to break. Three steps are involved in the calculation, which can lead to a higher amount of error.[19,29,30] Unpaired electrons cause great difficulties, which makes analyzing HEDMs even more challenging because they commonly form radicals. In small sets, BDE has been correlated to impact sensitivity, with the larger BDE leading to a less sensitive molecule, but when this is done on a large scale, the correlation drops.[29,30] The BDE does not consider the solid-state interactions that occur during the crystal that could lead to a change in sensitivity.

Bond indexes are another way to determine the trigger bond of the molecule. Our lab uses the Wiberg Bond Index (WBI) to analyze HEDMs.[23,24,31] The WBI is a measure of bond strength and is calculated by the sum of the square of the off-diagonal of the two-atom density matrix:[32]

$$\mathrm{WBI_{AB}} = \sum_{p\in A}\sum_{q\in B}\left(\mathrm{D_{pq}}\right)^2 \qquad (2)$$

The closer to either one, two, or three the WBI is for a particular bond indicates that it has more single, double, or triple bond characteristics.[32] It is similar to the overlap population but is not basis set dependent which reduces bias. This calculation also involves one step, leaving less room for error and reducing the computational cost. Using just the raw WBI can show how overlapped the electron density is, but to obtain a scale of bond strength as substitutions are made throughout the molecule, a reference molecule is needed that has the same atoms, bonding, and hybridization as the molecule that is being looked at.[23,24,31] The %WBI

$$\%\Delta\mathrm{WBI_{AB}} = \frac{\mathrm{WBI_{AB}(HEDM)} - \mathrm{WBI_{AB}(reference)}}{\mathrm{WBI_{AB}(reference)}} \times 100 \qquad (3)$$

Provides the scale needed to see the impact of the substitutions. Former lab members demonstrated that %WBI could be used to accurately determine the trigger bonds of novel HEDMs by first performing the calculation on RDX, HMX, TNT, TNB, and PETN, which are conventional explosives that have been studied extensively.[24] The predicted trigger bonds corresponded to the mechanisms of decompositions that have been accepted.[24] Then six novel HEDMs were tested in the same way and compared to mass spectrometry fragmentation, both of which agreed with each other.[24] It was determined that the trigger bonds have the most negative %WBI and the longest bond length in the molecule.[24] Shoaf performed another study of 63 nitroaromatic compounds using the %WBI.[23] This study showed that for nitroaromatics, the bond strength is influenced by the steric effects, ring strain, and electronic effects.[23] She also found that %WBI decreased as more nitro groups were added to the molecule.[23] However, it was also seen that %WBI predicts the trigger bond with the highest success if the classes of molecules are kept together.[23]

Predicting impact sensitivity and trigger bonds is a challenging task, especially with gas-phase single-molecule calculations. Most HEDMs are used in condensed phases and have the intermolecular interactions of the solid or liquid that can play a crucial role in the material's stability. Even though single-molecule calculations are computationally cheap, they ignore these contributions as well as the contribution from stimuli such as heat or pressure, which adds energy to the system and can cause different mechanisms to become attainable. Solid-state molecular dynamics simulations can be used to include these variables in the studies. Reactive Force Field (ReaxFF) is one technique that allows for pressure or heat to be sent as a shock wave through a unit cell of HEDMs to see what bonds will break or form with that stimulus.[33] One drawback of this technique, however, is the bonds must be defined, so the simulation will not count bonds if they are outside of the range which gives some bias to the calculation.[19,33] Density Functional Based Tight Binding (DFTB) is another molecular dynamics simulation that includes the band structure of the compound, short-range repulsions, long-range electrostatic forces, and Coulomb interactions.[34] It is more computationally expensive than ReaxFF but provides a more accurate picture of the molecules interacting with one another in the crystal.[19,34] Plane-wave Density Functional Theory (PWDFT) allows for the orbitals of the molecules to be defined, but then allows the simulation to determine bonds breaking and forming, reducing the bias in the calculations while also including the intermolecular interactions which allows for a more accurate calculation to be done and a computationally cheaper cost.[13,19] Our group has done simulations with PWDFT due to the decrease of bias in the calculation.

Building off previous research, my work focuses on determining the effectiveness of different computational methods and gaining insight into the mechanism of decompositions of compounds that have not been extensively studied. My first project used the %WBI method to determine the trigger bonds of azo compounds. The second project uses many methods to improve predicting impact sensitivity. Finally, the third project uses solid-state molecular dynamics simulations to study the effect that pressure has on HEDMs and to determine the threshold pressure needed to produce an explosion.

Methods

DFT Study

The optimization of 194 different HEDMs was done in the gas phase using Gaussian09[35] and the hybrid M06-2X26 functional and triple-ζ basis set augmented with polar functions (TZVP).[36] 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.[24] WBI calculations were done on the optimized structures through NBO analysis Version 3.1.[37] The dataset of molecules was selected from two papers that included the experimental h50 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.[38,39]

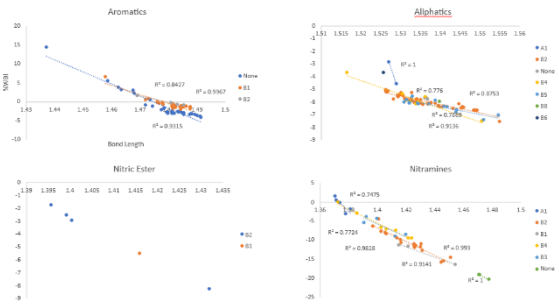
MM Study

The crystal structures of RDX, ammonium nitrate, TATB, and 1,1'-azobis(tetrazole) have been optimized using Quantum Espresso 6.1.[40,41] 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.[42]

Results and Discussion

DFT Study

In this study, 194 HEDMs were obtained from two papers, and all had experimental h50 values to compare to our calculations.[38,39] Wang et al. used three variations of an artificial nerve network (ANN) to create a quantitative structure-property relationship model for predicting the impact sensitivity of 156 molecules, the back-propagation neural network (BPNN), multiple linear regression (MLR), and partial least squares (PLS).[39] They inputted electropological-state values for the molecular structure descriptors and ran them through each network, producing a predicted h50.[39] 127 molecules from the dataset were used to build the model, and when plotted against the experimental h50, they obtained low R^2 values (R^2_{MLR}=0.7705, R^2_{PLS}=0.7659), which they then divided into three groups, nitramines and nitric esters,



nitroaromatics, and nitroaliphatics.[39] Grouping them increased their R^2 values to 0.7815-0.8522. When the entire dataset is plotted against the experimental h50s, an even lower R^2 is obtained (R^2_{MLR}=0.5818, R^2_{PLS}=0.5826), and the BPNN model that they were using as a comparison gave R^2=0.6198.[39] When the explosophores were grouped, R^2 values were calculated from 0.4142-0.7728, indicating that these models are not reliable on a large scale.[39] Mathieu and Alaime used all of Wang's dataset to train their model and added 39 molecules to use as their test sets.[38] In their study, the rate constant of propagating the decomposition was related to the h50, as one goes to zero, the other goes to infinity.[38] The 39 molecules were split into two groups, which when the predicted h50 was plotted against the experimental results, T1 and T2 gave R^2

values of 0.863 and 0.783 respectively.[38] However, when both sets were plotted together, R^2= 0.5216, indicating that this correlation works for molecules that are similar but cannot work with multiple explosophore types.[38]

Using Gaussian09[35,36,43], all 194 molecules were optimized using the hybrid M06-2X functional and a triple-ζ basis set (TZVP). TZVP was selected to avoid basis set dependence for our WBI by excluding diffuse functions.[24] Natural Bond Orbital (NBO) analysis version 3.1 was used to calculate WBI.[37]

Using %WBI, the trigger bonds were identified, and the molecules were split into nitroaromatics, nitroaliphatics, nitramines, nitric esters, and azo groups for further analysis. As the bond length increases, the %WBI decreases due to a reduction in the orbital overlap between the two atoms (fig 2). The number of hydrogen atoms α and β to the trigger bond's nitro group plays a role in the bond length and activation of the bond, explaining the three outliers in the nitroaliphatic group. The HOMO-LUMO gap was calculated for each molecule and compared to both the %WBI and the h50 and no correlation was found for any of the explosophores. For every group except the nitroaromatics, the dihedral angle of the trigger bond was not related to the sensitivity and activation. In the nitroaromatics, as the dihedral angle approaches 0°, the trigger bond becomes less activated, indicating that the strength of those bonds is dependent upon the p-orbital overlap more than the other explosophores. %WBI showed no correlation with oxygen balance for any of the groups.

The impact sensitivity was compared to the %WBI for each group, with no correlation being found for the nitramines and nitroaliphatics. For the nitric esters and nitroaromatics, a trend emerged that as the %WBI increased, the sensitivity increased as well. As there were only five data points for the nitric esters, further testing needs to be done to explore if the correlation is significant. In the case of the nitroaromatics, as the electron sharing is increased through the increase in π-bond character, the molecule stabilizes, increasing the h50, which was also shown with the dihedral angle, indicating that nitroaromatics depend significantly on the π-bonding characteristics of the trigger bonds.

Kamlet introduced a trend between the oxygen balance of the molecule and the ln(h50) in both nitroaromatic and nitroaliphatic compounds.[22] A slight logarithmic trend can be seen for each of the explosophore types; however, the correlation is not strong, indicating that other factors are also important when looking at the impact sensitivity. The addition of oxygen is typically done through the substitution of a nitro group. When the $\%NO_2$ of the molecule by weight is compared to the h50, a stronger correlation is seen (fig 3). With the addition of each explosophore on a molecule, the potential energy is increased until the

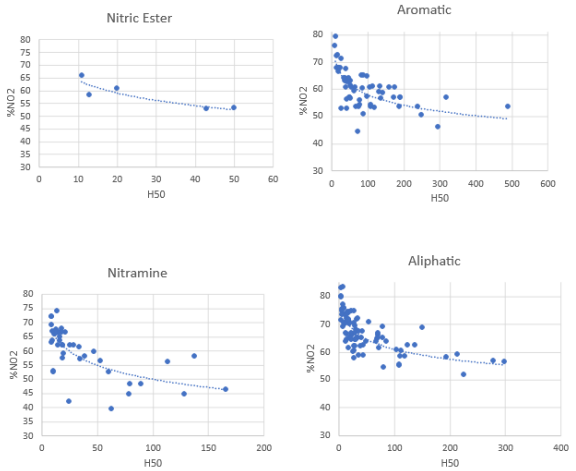


Fig 3. $\%NO_2$ displays a logarithmic trend with impact sensitivity for each of the different explosophores.

reaction proceeds on its own. The h50 values in this instance is similar to the activation energy of the reaction. The correlation for this is not experimentally significant either, even though it is stronger than oxygen balance, and more properties need to be included to account for electrostatic and steric interactions.

Using a larger dataset provides a more realistic view of the properties that affect impact sensitivity. Strong trends can be found with small datasets and selected molecules, but they do not hold up when looking at new molecules not used in trend-making. Impact sensitivity is complex and involves more than just the atomic composition of the molecule. More work should be done to identify the impact that each property has on the h50.

Molecular Dynamics Study

Ammonium nitrate (AN), first synthesized in 1654, is a common additive in fertilizers and is used as explosives and fuels.[44] Many accidents have occurred with AN, usually caused by improperly stored materials that begin to burn.[44] AN has five known crystal structures depending on the temperature, making understanding its decomposition challenging.[44] Many studies have been done with FTIR, TGA, DTA, and DSC, but these can only show the loss of functional groups and weight as temperature is increased, not the mechanism by which this happens.[44] Computational studies have become increasingly useful in seeing the effects of temperature on AN, but a consensus has not been reached on what the main mechanism/s is/are.[44] The effect of pressure on the reaction has not been looked at computationally, which is a crucial part in causing AN to explode.[44] Studies have been done experimentally where AN was heated in open and closed containers and allowed to react.[44] The open containers did not explode, but the sealed ones did, indicating that pressure and temperature are necessary to cause an explosion.[44]

RDX, TATNB, and azobistetrazole are newer HEDMs that are used today and have a better balance of safety and power than AN.[1] RDX has a N-NO_2 explosophore, TATNB has azide and C-NO_2 explosophores, and azobistetrazole contains an azo bridge.[1] By studying these compounds, a better understanding can be gained of how each explosophore type reacts to pressure.[1] The importance of pressure on these reactions can also be gauged and compared to that of AN's.[44]

Quantum Espresso will be used to perform simulations on the crystal structures of AN, RDX, TATNB, and azobistetrazole using plane-wave DFT.[40,41] The compounds will be compressed to varying pressures and then observed for any bond changes that would indicate a reaction had occurred. After the simulation's completion, ReacNetGenerator will be used to analyze the species that are formed from the pressure.[42] This experiment's results should show the importance of pressure on the decomposition of HEDMs and provide a threshold pressure to initiate an explosion. Several simulations have already been run, but the analysis remains to be completed. Additional simulations may be needed to locate the threshold pressure.

Conclusion

HEDMs are difficult to study experimentally, leading to computational studies being necessary. Single-molecule methods such as HOMO-LUMO gap, machine learning, and %WBI do not correlate enough with impact sensitivity to aid in predicting the property. OB does correlate with impact sensitivity, though the causation is still not fully understood. %WBI

can be used to predict the trigger bonds for some classes of HEDMs. Solid-state calculations are necessary to fully understand the contributions of these properties to the impact sensitivity as detonation is inherently a solid-state phenomenon.

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