Abstract. The chemical initiation of detonation in shock of highly unstable Si-PETN is explored through analysis of the intermolecular collisions that occur behind the shockwave front using first principles reactive molecular dynamics. The collisions are studied in terms of velocity, orientations, and reaction pathways. Threshold velocities indicate the most sensitive orientations, while bond dissociation energies were calculated and used to elucidate reaction pathways. The results are compared to those for PETN collisions and sensitivity patterns in terms of collisions are determined. Lastly, the relationship between the central atom silicon in Si-PETN and its increased instability is discussed.

Introduction

The study of detonation in energetic materials is one of much appeal and growing interest. Although much has been predicted about the macroscopic properties of the explosive reactions, there is a lack of understanding of the initial chemical reactions that occur behind the shockwave front. With the Chapman-Jouget model, the molecules were theorized to undergo the instantaneous transformation of reactants to products only at the shockwave front [1, 2]. Consequently, Zeldovich [3], von Neumann [4], and Doering [5] replaced it with the ZND model, which introduced a finite reaction rate and finite reaction zone. However, there is still much lacking in the study of these reactions on an atomistic level that concentrates on intramolecular interactions during the initiation.
Sila Penta-Erythritol Tetra Nitrate, or Si-PETN, is an extremely sensitive explosive molecule. Its structure consists of a central Silicon atom surrounded by four identical arms. Each arm extends from the central Si with its atoms arranged in the following manner: Si-CH$_2$O-NO$_2$-Si-PETN physically mirrors the much-studied explosive PETN, with the exception of having a central silicon atom rather than a central carbon atom. Si-PETN, however, is much more unstable than its carbon (PETN) counterpart [6]. It has been shown to explode upon contact with a spatula, and under a microscope [7]. While it has only been studied experimentally in solution, for the purpose of this experiment we assume that Si-PETN takes on the same crystal structure as PETN-I: a unit cell containing two formular units of crystal symmetry P-42$_1$c [8]. Comparisons between Si-PETN and PETN may reveal the reaction mechanisms responsible for the increased instability of Si-PETN.

In order to study the chemical dynamics initiated by the shockwave in energetic materials, it is assumed that the shockwave front compresses the crystal, and as a consequence of this compression, molecular collisions occur. Therefore it follows that bimolecular collisions can be used to determine the mechanisms of non-equilibrium chemistry that lead to Si-PETN instability.

**Computational Details**

To emulate these collisions, a single pair of molecules is selected from the Si-PETN crystal, preserving their relative orientation and position within the crystal. All possible collisions
between pairs in each crystallographic direction are predicted, while discarding redundant collisions. Each resulting pair is then placed in the center of a box, equilibrated at 300K, and half the desired velocity is then applied to each molecule within the box, with the molecules colliding as seen in Figure 1. The pair is used to simulate the collisions, and reactions are tracked by following the molecular dynamics of the trajectories at different speeds and crystallographic directions. MD simulations of the bimolecular collisions were performed using first principles DFT through Siesta calculations to determine reaction pathways and time scales.

The molecules were collided at speeds ranging from 2.00 km/s to 7.00 km/s. The collisions were performed with the molecules arranged in the following crystallographic directions: \{001\}, \{010\}, \{100\}, \{110\}, \{011\}, \{101\}, and \{111\}. Spheres of radius R, the radius of Si-PETN, were used to represent the molecules within the crystal, as arranged in Figure 2, while smaller spheres of radius R/2 were placed concentric to these. If the collisions involved the outer spheres only, they were labeled as glancing; if they included the inner spheres, they were labeled as head-on. Therefore, the collisions were classified by velocity, crystallographic direction, and as head-on or glancing.

Once the collisions were performed, the data obtained served to determine the types of products and their reaction times. The term threshold velocity refers to the minimum speed at both a specific orientation and direction in which the molecules involved will react after colliding with each other. Through these findings, one is able to project that the arrangements with the lowest threshold velocities are the most sensitive.
Some reactions were found to be unimolecular, where the molecules did not interact with each other, while others were bimolecular and showed mutual interaction in their product formation.

**Results and Discussion**

Various directions show differing threshold velocities as well as reaction pathways. The most sensitive orientations were \{001\} mol. 1-3 and \{110\} mol. 1-8, with threshold velocities of 3.10 km/s. The most insensitive collisions were \{100\} mol. 1-6 and \{101\} mol. 1-2 with velocities of 4.10 km/s and 5.10 km/s, respectively. As to whether there is a correlation between the velocities and the amount of products formed, it is shown that no relationship exists between the two. Although an initial assumption could be that collisions at higher velocities would generate more products, the simulations offer no evidence to support this. For example, the cases \{100\} mol. 1-6 and \{111\} mol. 1-2 have velocities of 4.10 km/s, and produce 6 fragments, but cases \{110\} mol. 2-3, and \{101\} mol. 1-2 with velocities of 4.5 km/s and 5.10 km/s, respectively, produce 2 and 1 fragments. Here the cases with lower velocities produced the higher amount of fragments. When variances in product formation within the same case are analyzed, there is no relationship between the collision velocity and product formation.

A comparison between the threshold velocities of Si-PETN and PETN offers much insight to the factors that determine sensitivity. Both compounds display having \{001\} and \{110\} as their most sensitive directions, while \{101\} and \{100\} are the most insensitive. Their threshold velocities are similar and follow the same trend. Since Si-PETN and PETN have the same molecular and crystalline structure, it is evident that sensitivity is closely linked to the crystal structure of the molecules. The different central
atoms of the two molecules do not seem to affect the structures’ identical trend in sensitivity. Furthermore, there were no observed differences between head on collisions and glancing collisions.

The reaction pathway after collisions of Si-PETN followed a pattern where NO$_2$ dissociation occurred first in all cases, proceeding with the breaking of the Si-C bond of the same arm and an expulsion of formaldehyde. Multiple NO$_2$ dissociations occurred in some cases, as well as multiple expulsions of formaldehyde. Bimolecular collisions showed the formation of products involving the long range bonding capabilities of the central silicon atom. As an explanation to the most observed pathway (formation of NO$_2$ product followed by CH$_2$O), the bond dissociation energies of the bonds in question were calculated. The lowest BDE was found to be that of the O-NO$_2$ bond, at a value of 158.59 kJ/mol. This BDE proved to be the lowest of all bonds, which provides a clear explanation for the consistent release of NO$_2$. The BDE for the C-S bond that attaches the arm and the rest of the Si-PETN molecule is 230.68 kJ/mol. However, once the O-NO$_2$ bond is broken, the BDE of the C-S bond previously mentioned greatly lowers from 230.68 kJ/mol to 81.64 kJ/mol. This shows that breakage of the C-S bond and the separation of formaldehyde is therefore the next ideal reaction, rather than the formation of other NO$_2$ molecules. It is important to note that PETN follows this exact pathway, exhibiting the same decrease in the bond dissociation energy of the C-C bond as Si-PETN experiences in its S-C bond. Further proof that the structure of the molecules, rather than its components, plays a key role in sensitivity and reaction dynamics.
A unique characteristic of Si-PETN is its formation of an S-O bond through a so-called “oxygen attack”. The expansion of the Silicon's coordination geometry from four to higher allows for a transition state where an S-O bond exists simultaneously with the four S-C bonds. This characteristic has been shown to be responsible for the much larger instability of Si-PETN compared to PETN. Si-PETN is more capable of forming a bond between oxygen and its central atom than PETN, and as a consequence, creates a highly exothermic reaction through the formation of this Si-O bond. The effects of this oxygen attack can be seen in the collision \{010\} mol. 2-6, where one of the molecule’s arms becomes inverted after NO\textsubscript{2} scission. After the O-NO\textsubscript{2} bond is broken from one arm; the central silicon undergoes a transition state during which the oxygen of this arm bonds with the silicon, as the silicon is bonded with the four carbon atoms of each arm, as displayed in Figure 3c. Following the transition state, the carbon bonded to the silicon breaks its S-C bond, and a reversal of this arm is observed. The resulting molecule then proceeds to separate into other fragments. Figure 4 offers a plot of the bond lengths of the

![Figure 3](image1.png)  
**Figure 3.** Progression of collision with oxygen attack. Note that frame b shows five coordinate transition state for silicon.

![Figure 4](image2.png)  
**Figure 4.** Bond lengths of Si-C and Si-O bonds. Note that five-coordinate transition state occurs at intersection.
Si-O and Si-C bonds, with the point of intersection marking the instant where the five coordinate transition state occurs.

Bimolecular collisions resulted in the formation of two molecules, one where the two molecules are linked by formaldehyde after each losing an arm, shown in Figure 5, and another where the two molecules are linked through an Si-Si bond after also losing an arm. Entropy calculations for these structures are currently under progress, but thus far they seem to be stable.

**Conclusions**

Both Si-PETN and PETN have similar sensitive directions. Threshold velocities were similar for both, with Si-PETN having slightly lower velocities. However, the trends these velocities follow with respect to orientation and direction are identical. Sensitivity is thus more closely related to crystalline structure and molecular structure than to the properties of the individual atoms involved in the molecules.

Si-PETN and PETN both show the same primary reaction pathway: release of NO$_2$ followed by H$_2$CO. In the two cases, the release of NO$_2$ is due to this bond’s low dissociation energy. The separation of formaldehyde is caused by a sharp decrease in the Si-C BDE after the NO$_2$ scission. Si-PETN differs from PETN in the sheer amount of products formed, which is considerably higher than those for PETN. This is linked to Si-PETN’s instability.
The instability experienced by Si-PETN can be attributed to the central silicon’s readiness for long range interaction with other atoms and its ability to undergo a transition state. While PETN’s reactions were always unimolecular, Si-PETN experienced both bimolecular and unimolecular collisions. These resulted in the formation of products composed of a combination of the colliding molecules. The transition state, in turn, was responsible for facilitating Si-O bonding within the molecule.

The notable similarities shown by Si-PETN and PETN through the collision simulations offer proof that crystalline structure is a determining factor for sensitivity. Specific components of these molecules affect product formation. Therefore it is instability rather than sensitivity what differentiates Si-PETN from PETN.

References

1. D.L. Chapman, Philos. Mag. 47, 90 (1899)
2. E. Jouget, J. de Mathematiques Pures et Appliquees 1, 347 (1906)
4. J. von Neumman, Office of Science Research and Development: Report No. 547 (1942)
5. W. Doering, Ann. Phys. 43, 421 (1943)