Multiple Reaction Pathways in Shocked 2,4,6-Triamino-1,3,5-trinitrobenzene Crystal

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Supporting Information

ABSTRACT: Detonation processes probed with atomistic details have remained elusive due to highly complex reactions in heterogeneous shock structures. Here, we provide atomistic details of the initial reaction pathways during shock-induced decomposition of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) crystal using large reactive molecular dynamics simulations based on reactive force fields. Simulation results reveal the existence of three competing intermolecular pathways for the formation of N₂. We also observe the formation of large nitrogen- and oxygen-rich carbon aggregates, which delays the release of final reaction products.

INTRODUCTION

Many organic high-explosive (HE) materials are metastable molecular solids composed of C, H, N, and O atoms. During detonation, HE materials produce stable small molecules such as N₂, H₂O, and CO₂ via complex chemical reactions and release excess energy. The time scale of these detonation processes varies widely from nanoseconds to microseconds, depending on the molecular composition and physical properties (e.g., density and crystal structure) of HEs as well as chemical reaction pathways involved in the decomposition processes. However, these processes are very difficult to understand with atomistic detail.

2,4,6-Triamino-1,3,5-trinitrobenzene (TATB with chemical composition C₆H₆O₆N₆, shown in Figure 1a and 1b) is an extremely insensitive yet moderately powerful polyamino-polynitro arene HE material. Its unusual thermal and shock resistances, as well as its chemical stability, make TATB highly important technologically. Due to the interplay of covalent bonds with hydrogen bonds and van der Waals interactions, reactivity of TATB under shock is also a fundamental scientific problem. Understanding its chemical reaction during the detonation process with atomistic detail may provide insight about the chemical stability of TATB and eventually leads to the discovery of safer and more powerful HE materials. Thus, both the thermal and the shock stability of TATB have been studied in great detail by both experiment and theory.

In a TATB molecule, the C−NO₂ bond dissociation energy is much lower than the C−NH₂ bond energy. Thus, loss of nitro groups via various possible mechanisms was suggested as a primary pathway. Sharma et al. observed the loss of NO₂ via scission of C−NO₂ bonds as the primary pathway during thermal and photoinduced decomposition. Shock and impact studies by Sharma et al. suggested the formation of benzoquaran or benzofoxyan intermediates. First-principles electronic structure calculations by Wu et al. suggested that intramolecular hydrogen bonding plays a crucial role in the thermal decomposition of TATB. Hydrogen-transfer-mediated ring closure leads to the formation of benzoquaran or benzofoxyan intermediates. Simultaneous thermogravimetric-modulated beam mass spectrometry and time-of-flight velocity spectra measurements also observed the formation of benzoquaran derivatives.

In contrast to these studies, other spectroscopic and thermal studies by Makashir and Kurian suggested C−NH₂ scission as the primary reaction step. Farber and Srivastava suggested a carbon-ring cleavage mechanism for the thermal decomposition of TATB. Another study using time-of-flight mass spectroscopy by Östmark suggested the formation of nitroso compounds in subdetonation of TATB. On the contrary, reactive force field simulation for the thermal decomposition of TATB suggested the presence of more than one mechanism. Shock decomposition pathways of crystalline TATB were studied by Manna et al. using molecular dynamics (MD) simulations based on the density functional tight binding (Scc-DFTB) method, which also confirmed the presence of nitrogen-rich mono- and dibenzoquarans heterocycles.
for the formation of these final compounds are in subnano-second due to the formation of these heterocyclic compounds. These clusters act as reactivity retardants, leading to the shock insensitivity of TATB. However, the formation of these heterocyclic clusters under shock and impact is not well understood, especially within complex heterogeneous shock structures.

Such complex reactions in realistic shock structures can now be studied by large-scale reactive molecular dynamics (RMD) simulations based on first-principles-derived reactive force fields (ReaxFF). \(^{25}\) We use ReaxFF-lg, ReaxFF with dispersion correction. ReaxFF-lg has been tested for several HEM such as RDX, PETN, and TATB. ReaxFF-lg provides a relatively better equation of state of TATB than ReaxFF. ReaxFF-lg also provides a better ground state description (such as heat of sublimation, density, and cell parameters). \(^{26–28}\) We study shock-induced decomposition of TATB with atomistic detail. Simulation results provide understanding about the controversial C–NH\(_2\) and C–NO\(_2\) bond scissions as well as the formation of N\(_2\) and H\(_2\). We identified intermolecular pathways for the formation of N\(_2\) and H\(_2\). We also observed the formation of a large carbon cluster with high nitrogen and oxygen contents.

**RESULTS AND DISCUSSION**

At time \(t = 0\), the flyer starts to move toward the TATB crystal and compresses it, while the repulsion between the flyer and TATB decelerates the flyer. After compression for 10 ps, the repulsive flyer starts to retreat. In the compressed TATB crystal, high temperature and pressure trigger exothermic reactions via chemical decomposition. A supersonic detonation wave from decomposition of TATB travels through the crystal with a speed of 9.98 ± 0.5 km/s. A shock front is clearly identified as a discontinuity in temperature and pressure profiles as shown in Figure S1 in the Supporting Information. \(^{29}\) Earlier calculation by Manna et al. suggests that hotspot chemistry initiate between 8 and 9 km/s. \(^{24}\) Reaction products jet out toward left as shown in Figure 1c. Figure 1d shows the temperature profile as a function of the position along the \(a\) axis and time. As the flyer hits the TATB crystal, the temperature rises rapidly and a shock wave travels through the TATB crystal. The sharp interface between the unreacted (colored blue) and fully/partially reacted (green/red) regions signifies a shock wave passing through the system. The shock wave reaches the end of the system in ∼10 ps, and the right end of the system starts to heat up due to a rarefaction wave. The fully reacted system expands toward the left empty space as shown by the leftmost red region in Figure 1d.

To study chemical reaction pathways, we perform a fragment analysis. A bond is defined by a unique cutoff value of bond order for each atom pair. \(^{26}\) A cluster of atoms, connected with covalent bonds, constitutes a molecule. Figure 2 shows the number of molecular products formed as a function of time. Final products include N\(_2\), H\(_2\)O, CO\(_2\), and C as shown in eq \(^1\). \(^{30}\)

\[
\text{C}_9\text{H}_6\text{N}_8\text{O}_6 \rightarrow 3\text{H}_2\text{O} + 3\text{N}_2 + \frac{3}{2}\text{CO}_2 + \frac{9}{2}\text{C}
\]

H\(_2\)O is the first product to form. After that we observe the rapid production of both N\(_2\) and H\(_2\). Unlike in similar HEMs such as RDX and HMX, CO\(_2\) is the dominant product compared to CO. \(^{25}\) We observe NH\(_3\) formation at the initial phase. However, the number of NH\(_3\) fragments remains nearly constant after the initial transient. Therefore, NH\(_3\) was not included as part of the final products. Similar behavior was observed during the thermal decomposition of TATB by Quenneville et al. \(^{30}\)

The time constant for the formation of a product can be estimated by fitting the corresponding number of molecular fragments in Figure 2 to an exponential form as a function of time by using balanced reaction formulas.
observed during the thermal decomposition of nitromethane. This pathway has been suggested for the formation of N$_2$ in RDX and HMX.$^{3,32,33}$ NH$_3$ from C–NH$_2$ bond scission can form ammonia as the final product by abstracting another hydrogen from N–H bond or form N$_2$ by recombination with other NH$_3$ or NO$_2$ groups. Experimental studies of high-temperature thermal decomposition of TATB show the formation of NH$_2$.

To further understand the mechanism behind the formation of N$_2$, we trace back the initial environment of constituent N atoms. We count the number of N$_2$ molecules formed from different possible combinations, i.e., NH$_2$–NH$_2$, NO$_2$–NH$_2$, and NO$_2$–NO$_2$ pairs. These three pairs represent three different intermolecular reaction pathways I, II, and III, respectively. Table 1 shows the percentage of N$_2$ molecules that are formed from different reaction pathways after 40 ps. Surprisingly, we observe that 50% of N$_2$ is formed from NO$_2$–NH$_2$ pairs during shock decomposition. The high percentage of N$_2$ formation from NO$_2$–NH$_2$ pairs may be due to the spatial proximity of NH$_2$ and NO$_2$ groups in the crystal. In TATB crystal, a NH$_3$ group from a TATB molecule is adjacent to a NO$_2$ group from another TATB molecule as shown in Figure S4. As we compress the TATB crystal in the a crystallographic direction, the distance between NH$_2$ and NO$_2$ pairs decreases drastically. This may be the reason for reaction pathway II via NO$_2$–NH$_2$ being the dominant reaction pathway. Depending on the shock direction in TATB crystal, the reactivity and the primary chemical reaction may change.$^{14}$ In HMX and RDX, N$_2$ products are formed from NO$_2$–NO$_2$ pairs. However, N$_2$ formation from NO$_2$–NO$_2$ pair is very low in the case of TATB. While it is clear that NO$_2$–NH$_2$ pair dominantly produces N$_2$ from Table 1, the other reaction pathways cannot be ignored quantitatively, namely, reaction pathways I and III via NH$_2$–NH$_2$ and NO$_2$–NO$_2$ pairs produce the remaining 50% of N$_2$.

In fact, the first step in the shock decomposition of TATB crystal is compressive formation of large clusters from the coalescence of multiple TATB molecules. During the coalescence process, H$_2$O molecules are released. Due to the extreme compression, we observe the distortion of the planar benzene rings in all three pathways. Detailed analyses suggest that reaction pathways diverge to different reaction pathways to form N$_2$ from different fragment pairs as shown in the Supporting Information videos.$^{27}$ The three videos show the formation of N$_2$ from reaction pathways I, II, and III. (Though TATB molecules are usually in a large cluster, the complete cluster is not shown in the videos for the clarity of presentation.)

Reaction pathway I (from NH$_2$–NH$_2$ pair) to form N$_2$ undergoes transformation via C–NH$_2$ bond scission from two different TATB molecules. After distortion of the planar structure, the C–NH$_2$ bond breaks to form two NH$_2$ species. Subsequently, the two NH$_2$ groups are combined to form N$_2$. C–NH$_2$ bond breaking has been observed experimentally.

![Figure 2. Number of molecular fragments formed as a function of time for shock speed 9.98 km/s.](Image)

![Table 1. Percentage of N$_2$ Formed from Different Fragment Pair after 40 ps](Image)
under high static pressure. During this process, hydrogen is abstracted by OH or other NH2 species to form H2O or NH3, respectively. The dissociation energy for the C−NH2 bond is very high compared to that of the C−NO2 bond, but spectroscopic studies suggest that hydrogen bonding with the C−NO2 group weakens the C−NH2 bond. The presence of NH3 has been experimentally observed, which suggests the presence of this pathway. Even though it is not a primary reaction pathway, it accounts for 28% of the production of N2.

Reaction pathway II (from NH2−NO2 pair) is found to be the primary channel for the production of N2, accounting for 50% of the total N2 produced. The first step in this channel is the loss of oxygen assisted by an intramolecular/intermolecular NH2 group. Oxygen loss was also reported experimentally in the decomposition of TATB molecules. NO species react with nearby NH2 groups from other TATB molecules to form N2 and H2O/OH. Hydrogen and oxygen are abstracted by OH and NH2 species to form water and ammonia. This reaction pathway was also observed in quantum molecular dynamics studies performed by He et al.

Reaction pathway III (from NO2−NO2 pair) contributes only 22% in the formation of N2. This reaction starts with the breaking of the C−NO2 bond from two nearby TATB molecules. We also observe the presence of NO2 as an intermediate in shock decomposition of TATB. Two NO2 species form N2 as a final product. C−NO2 bond breaking has been observed experimentally under high static pressure.

To understand the timeline of these reactions, Figure 3 shows the fraction of N2 formed from different reaction pathways as a function of time. The figure shows that the NH2−NO2 pathway (reaction pathway II) dominates over the other two pathways (reaction pathways I and III). Reaction pathway III dominates over reaction pathway I in the early stage of the reaction, since the C−NO2 bond energy is lower than the C−NH2 bond energy. Thus, N2 formation via reaction pathway III is higher. However, after 3 ps, reaction pathway I becomes the most favorable reaction pathway. Experimental studies of photoinduced decomposition of TATB at ambient and high pressures by Glascoe et al. suggest that elevated pressure may inhibit the hemolysis of the C−NO2 bond and block the primary decomposition process.

Finally, we perform the stoichiometric analysis for the large clusters. Figure 4a shows the fraction of the number of atoms in large clusters with respect to the total number of atoms. Here, a large cluster is defined as a cluster that contains more than 24 atoms. The number of large clusters increases rapidly first as the flyer starts to compress TATB crystal. When the rarefaction wave returns, the fraction of large clusters increase again. After 20 ps, the number of large cluster starts to decline.

Figure 4b shows the carbon-to-oxygen (red line) and carbon-to-nitrogen (blue line) ratios in the large clusters. We observe that large clusters are nitrogen and oxygen rich, which delay the formation of stable products such as N2, CO2, and H2O in later stages. Most of the final products seep out of these large clusters. Quantum molecular dynamics studies by Manna et al. found the presence of nitrogen-rich clusters, which impede the formation of N2. Oxygen-rich clusters were also reported in shock simulation of RDX and thermal decomposition of TATB.

**CONCLUSION**

In summary, our RMD simulations reveal that N2 production in shock decomposition of TATB is a multichannel process. Reaction mechanism studies suggest that a reaction pathway via NH2−NO2 pairs is the primary reaction pathway for the formation of N2. However, other two pathways (from NH2−NH2 and NO2−NO2 pairs) also participate significantly in the formation of N2. Primary reaction stages include the formation of N2 and H2O rapidly and then somewhat slower formation of CO2. Most of the products formed via intermolecular pathways.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b05253. Intermediate analysis and shock speed analysis (PDF)

Movie for formation of N2 from reaction pathway I (AVI)

Movie for formation of N2 from reaction pathway II (AVI)
Movie for formation of N₂ from reaction pathway III (AVI)

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(29) See Supporting Information for simulation methods and details.
