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Atomistic Simulations of Chemical Reactivity of TATB Under Thermal and Shock Conditions

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Abstract. We performed quantum molecular dynamics simulations to study the reactivity of triamino-trinitrobenzene (TATB) crystals under thermal and shock conditions. For thermal decomposition of TATB, we conducted constant volume-temperature simulations, ranging from 0.35 to 2 nanoseconds, at $\rho = 2.87 \text{ g/cm}^3$ at $T = 3500, 3000, 2500, \text{ and } 1500^\circ \text{ K}$, and $\rho = 2.9 \text{ g/cm}^3$ and 2.72 g/cm^3 at $T = 3000^\circ \text{ K}$. We also simulated crystal TATB's reactivity under steady overdriven shock compression using the multi-scale shock technique with specified shock speeds of 8, 9, and 10 km/s for up to 0.43 ns duration. Both thermal and shock decomposition simulations enabled us to track the reactivity of TATB well into the formation of several stable gas products, such as H_2O , N_2 , and CO_2 . Although complex chemical transformations are occurring continuously in the dynamical, high temperature, reactive environment of our simulations, a simple overall scheme for the decomposition of TATB emerges: Water is the earliest decomposition products to form, followed by a polymerization (or condensation) process in which several TATB remaining fragments are joined together, initiating the early step in the formation of high-nitrogen clusters, along with stable products such as N_2 and CO . Remarkably, these clusters with high concentration of carbon and nitrogen (and little oxygen) remain dynamically stable for the remaining period of the simulations. Our simulations, thus, reveal a hitherto unidentified region of high concentrations of nitrogen-rich heterocyclic clusters in reacting TATB, whose persistence impede further reactivity towards final products of fluid N_2 and solid carbon. A reduced five steps, global reaction mechanism with Arrhenius kinetic rates for the decomposition of TATB, along with comparative Cheetah decomposition kinetics at various temperatures have been constructed.

Introduction

Key aspects in energetic materials research are the determination of kinetics and transport properties for the vast chemical transformations

that occur on very short time-scales at high-pressure and temperature. Subjected to conditions of up to 40 GPa in pressure and 6000° K in temperature, such as the case maybe under shock-waves compression, chemical reactions start to

occur in a few picoseconds, as recent molecular dynamics studies on energetic materials have revealed,^{1,2} with reaction times to completion, inferred from hydrodynamic measurements, ranging from few nanoseconds to as many microseconds. A major shortcoming of current high explosives (HEs) models is the lack of chemical kinetics data of the reacting materials at these conditions of high density and temperature. Experimental diagnostics, spectroscopic or otherwise, face the dire prospects of unraveling ultrafast materials transformation in a complex process of such an extended duration. Atomistic molecular dynamics simulations with reactive chemistry have emerged as an alternative recourse to obtain decomposition mechanisms and kinetics information in order to develop improved macroscopic models of explosives reactivity.¹⁻³

It has been noted that explosives rich in carbon tend to have much longer reaction zones than those that do not. Such explosives form graphitic or diamond-like carbon particles during detonation.^{4,5} Formation of the bulk carbon solid from the clusters is believed to play a key role in determining the size of the reaction zone of a given explosive.^{4,6} The latter process is thought to be initiated by collecting carbon atoms from a relatively large volume and governed by diffusion-limited growth of these clusters. TATB ($C_6H_6N_6O_6$) is an insensitive explosive with an estimated reaction zone in the microsecond regime. It can be described as markedly under oxidized, or alternatively, carbon rich. As a consequence, significant carbon formation in some form (graphite, clusters, or diamond) is expected to be part of its final products under detonation reactions.

In this work, we use quantum based molecular dynamics simulations to model the reactivity of TATB under thermal and shock conditions. Unlike reactive force fields, quantum based methods permit us for the first time to examine electronic properties at detonation conditions. Relatively few studies have been performed on the chemistry of stronger shocks due to the more challenging timescales involved and requirement for accurate methods of simulating a variety of chemical reactions, and our reported simulations are the first to probe the formation of stable products in an insensitive high explosive under conditions of a

steady shock. Our thermal and shock simulations allow us to (a) incorporate high-pressure reaction rates in thermochemical-hydro-codes to simulate TATB reactivity under various scenarios, including grain-scale dynamics, (b) enhance thermo-chemical codes capabilities by providing a complete account of relevant species, and (c) obtain a “reduced” reaction sets from insight into detailed decomposition pathways. In addition, our simulations have revealed an important feature of TATB decomposition: the first evidence for the formation of an extended region of nitrogen-rich heterocyclic clusters, the formation of which inhibits reactivity towards final decomposition products of fluid N_2 and solid carbon.⁷ This result suggests a new mechanism for carbon-rich explosive materials that precedes the slow diffusion-limited process of forming the bulk solid from carbon clusters. Another important feature undisclosed previously in the reactivity of energetic materials at extreme conditions is the prevailing persistence of small charged species through out thermal and shock simulations.

Methods

For reactive molecular dynamics simulations, two approximations are usually compulsory. The first is that the motion of the ions is assumed to be classical and follows Newton’s second law. The second approximation is concerned with the type of potential that governs the interatomic interactions. In this work, we use a quantum-based semi-empirical methodology, the Self-Consistent Charge Density-Functional Tight Binding (SCC-DFTB) method.⁸ The SCC-DFTB method is an extension of the standard tight binding approach in the context of density functional theory, allowing for the description of total energies, atomic forces, and charge transfer in a self-consistent manner. Therefore, charged, ionic, transient or otherwise species can be accounted for within this methodology.

Thermal decomposition simulations were conducted at constant-volume and temperature. Periodic boundary conditions were imposed in all directions, while constant temperature conditions were implemented through simple velocity rescaling. The probability to rescale atom

velocities was chosen to be 0.1 per time step. A dynamic time-step of 0.48 fs was used. Several simulations with various density, size, and temperature were carried out: (1) four simulations used a 1X1X3 supercell (144 atoms) at density $\rho=2.87\text{ g/cm}^3$, corresponding to an initial pressure of 29.7 GPa was thermally heated at various temperatures of $T=3500, 3000, 2500, \text{ and } 1500^\circ\text{ K}$, and (2) two simulations used a 2X2X1 supercell (192 atoms) at two densities $\rho=2.72$ and $\rho=2.9\text{ g/cm}^3$, corresponding to initial pressures of about 22 and 34.5 GPa, respectively, were thermally heated at $T=3000^\circ\text{ K}$. These simulations varied in duration from 400 ps to 2.0 ns.

We simulated crystal TATB's reactivity under steady overdriven shock compression using the multi-scale shock technique.^{9, 10} In this molecular dynamics (MD) method, equations of motion for the atoms and volume of the computational cell are time evolved subject to stress and energy constraints satisfying a continuum description of the shock wave. Since the computational cell of the multi-scale technique follows a Lagrangian point through the shock wave, it enables a simulation of a system experiencing a shock wave with far fewer atoms than normally required. We performed MD simulations with a time step of 0.5 fs for up to 430 ps with shock speeds of 8 and 9 km/s, and 202 ps for a shock speed of 10 km/s on the 1x1x2 smaller computational cell. For the larger 1x2x2 supercell, the simulation was conducted up to 140 ps. In all simulations, initial position of TATB molecules were taken from the experimental x-ray structure, and then optimized with the SCC-DFTB method. Initial velocities were randomly chosen, with an initial temperature of 300° K . We then performed an equilibration for a period of up to 2 ps at temperature of 300° K . Shock compression occurred along the c (z) lattice direction in all simulations.

Fast chemistry at 10^{-15} second scale requires elaborate and robust identification of molecular species. We implemented a procedure to identify stable molecular species based on bond-length and lifetime criteria: two atoms were counted as bonded if their distance was less than a critical value r_c . For atoms bonded to hydrogen the distance criterion must be met for at least 20 fs,

while bonds not involving H (e.g. C-C, N-O, etc.) must survive 45 fs. These timescales were chosen to be characteristic of a few molecular vibrations. r_c was determined to be the first maximum in the calculated element-element potential of mean force. Further, molecules were required to meet a minimum lifetime of 100 fs before being identified.

Results

Experimentally observed TATB detonation velocity is 7.7 km/s at $\rho=1.88\text{ g/cm}^3$ and a pressure of 29 GPa.¹¹ In our shock simulations, TATB must be substantially overdriven to observe chemistry on sub-ns timescale. Figure 1 displays the time evolution of the average temperature, stress, and volume for all three initial shock speeds.

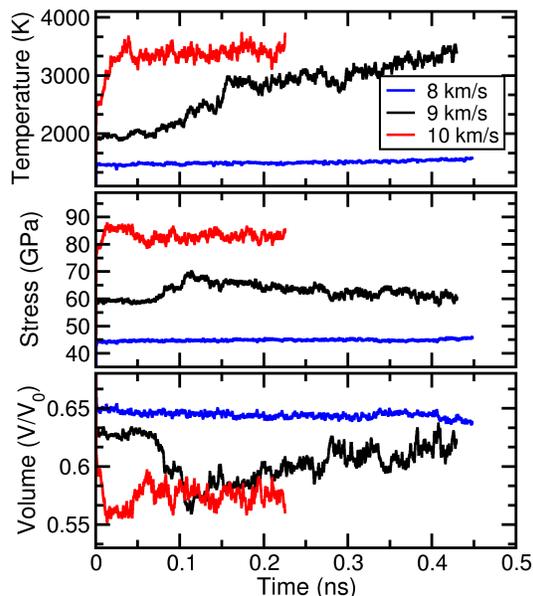


Fig. 1. Time evolution of average temperature, shock-propagation-direction stress, and volume of 1x1x2 computational cell for simulations at shock speeds of 8, 9, and 10 km/s.

For the 9 km/s shock speed simulation, the temperature gradually increases from around 1900 to 3500° K , while the stress increases from 58 to 70 GPa. This is due to recurring chemical

reactions. More dramatic conditions are noted for the 10 km/s shock speed simulation, where the temperature increases from around 2500° K to 3500° K at half the simulation duration of the 9 km/s shock speed, and the stress reaches 85 GPa in less than 50 ps of simulation time. For the 8 km/s simulation, the temperature and stress maintain near constant values of 1500° K and 42 GPa throughout the simulation period. The only observed reactivity at this shock speed is protons transfer between amino and nitro groups up to 0.43 ns of simulation time. A similar observation is obtained from thermal heating at T=1500° K up to 2 ns. These results clearly indicate that chemical transformations occur faster as the temperature increases (or shock speed increases).

The use of quantum based methods permit us for the first time to examine electronic properties at detonation conditions. Our recent simulations of shocked nitromethane showed that a transient band-gap reduction to a semi-metallic state occurred during shock compression with a speed of 6.5 km/s.¹² Our shock simulations of TATB also show a non-monotonic change in electronic properties. Figure 2 compares the dimensionless electronic state overlap parameter, which is often used to characterize metallization,¹³ of TATB and detonating nitromethane. With an overdriven shock speed of 9km/s, TATB is in a metallic state throughout most of the simulation. For a shock speed of 8 km/s, it stays mostly as an insulator, which is consistent with its lack of reactivity.

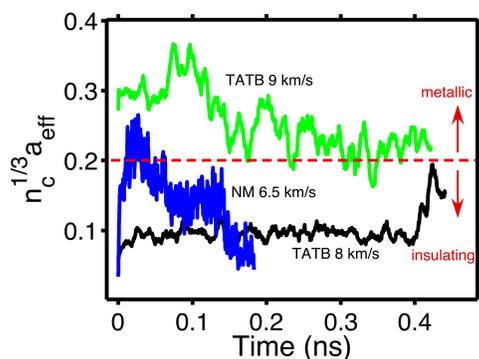


Fig. 2. Time profile of the electronic state overlap parameter $n_c^{1/3} a_{eff}$ for TATB and nitromethane. n_c is the charge-carrier concentration, and a_{eff} is the effective Bohr radius of electronic states.

Global features of TATB decomposition obtained from both thermal and shock simulations revealed similar trends. The shock simulation with a speed of 9 km/s has a temperature range of about 1900-3500° K, allowing for comparison with thermal decomposition simulations within T=2500-3500° K. Fast chemical transformations, particularly at high T (e.g. T=3500° K) are in common. At this temperature, H₂O and N₂ dominant gas formation occurred in less than 100 ps, with water being first to appear. At the high T condition, dissociation-recombination reactions of the type H₂O ↔ H + OH are very prevalent. Furazan-like structures seem to accompany H₂O formation. Once hydrogen is eliminated from amine groups to form water, nitrogen of adjacent molecules joins in to form N₂.

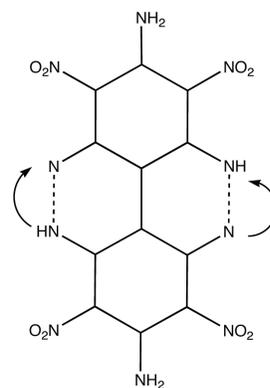


Fig. 3. Condensation reactions (e.g. bimolecular) to form N-N bonds from parent fragments.

Unlike water, however, the formation of N₂ does not proceed before a polymerization process is underway in which the heavy fragments of the parent TATB have bonded together, as illustrated in figure 3. Nitrogen formation can thus be described as having several growth steps: (1) elimination of H₂O and NO with furazan-like structures as intermediates, (2) formation of extended ring network (condensation reactions), and (3) later steps are always preceded by ring formation with N-N or N-N-N. It should be noted that experimental evidence for benzofurazans formation have been reported for decomposing

TATB subjected to various stimuli such as heat, impact, or UV photolysis.¹⁴

Fast chemistry in our thermal and shock simulations is also exhibited by the fact that both H₂O and N₂ appear to reach steady state of concentration at about 100 ps and 250 ps, respectively. Figure 4 displays the concentration profile of TATB and most dominant, stable products from the shock simulation with a speed of 9 km/s. Figure 5 shows the concentration profile of water from thermal decomposition simulations of two temperatures, T= 2500, and 3500° K at $\rho= 2.87 \text{ g/cm}^3$, along with an exponential fit to obtain reaction rates of this product.

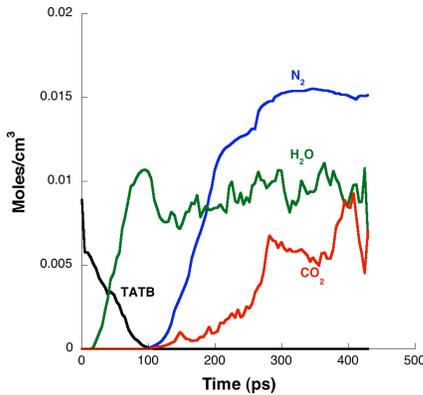


Fig. 4. Concentration time profile of TATB and dominant gas products N₂, H₂O and CO₂, from the simulation with shock speed of 9 km/s.

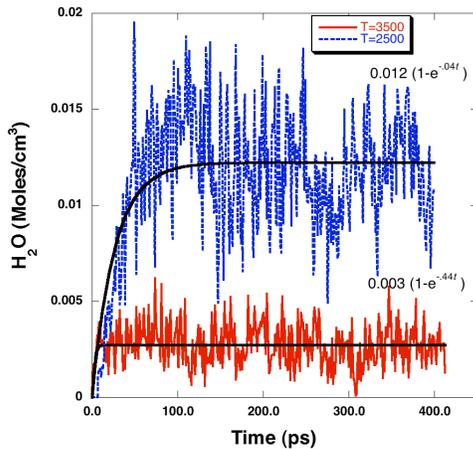


Fig. 5. Water concentration profile from thermal decomposition simulations at T=2500 and 3500° K.

We found that concentration profiles of stable products such as H₂O and N₂ can be fit to an expression of the form: $C(t) = C_{\infty}(1 - e^{-bt})$, where C_{∞} is the equilibrium concentration and b is the effective rate constant. From this fit to the data in figure 5, we estimate effective reaction rates for the formation of H₂O to be 0.04 and 0.44 ps⁻¹ for T=2500 and 3500° K, respectively. The shock simulation with a speed of 9 km/s also provides a similar fit for H₂O, and an effective rate of 0.02 ps⁻¹. A similar fit for N₂, as shown in figure 6, at T=3500° yielded an effective rate of 0.11 ps⁻¹. The figure presents the N₂ concentration profile from thermal simulations at T=2500 and 3500° K, and from the shock simulation (insert). We note the similarities in N₂ delayed formation at T=2500° and the shock simulation, along with its step-type formation due to “condensation reactions” of the type shown in figure 3 above.

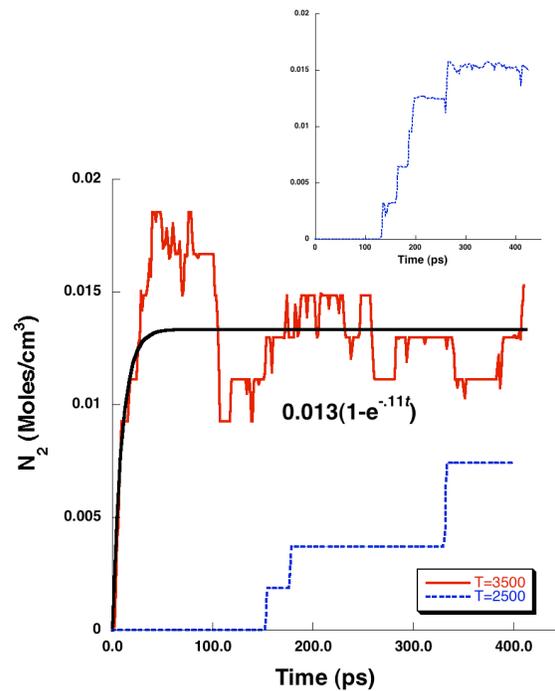


Fig. 6. N₂ concentration profile from thermal decomposition simulations at T=2500 and 3500° K at $\rho= 2.87 \text{ g/cm}^3$, and shock simulation with speed of 9 km/s (insert).

Our thermal and shock simulations revealed a very important step in TATB decomposition process: the formation of carbon-rich, nitrogen-rich heterocyclic clusters of various sizes. In figure 7, we compare the results obtained from simulations of cell sizes of 1x1x2 and 1x2x2 for the shock simulation with a speed of 10 km/s. The plot shows the time profile of the average nitrogen to carbon ratio in carbon-containing clusters. As shown, both simulations confirm the formation of nitrogen-rich heterocycles, albeit at different time due to increased reactivity with increase in the shock speed. Figure 7 also shows the nitrogen contents variation in these clusters, ranging between 50% N and 100% N in the smaller cell simulation, and between 63 % N and 96% N in the larger 1x2x2 simulation cell. In all of our thermal simulations we found that the formation of these heterocycles is persistent so much that no further decomposition occurred, even at the highest temperature. For example, the formation of high N clusters persists from ~50 ps to 0.42 ns at T=3500° K. This is a testament to the resiliency of these clusters towards further decomposition and further retardation of chemical reactivity of TATB.

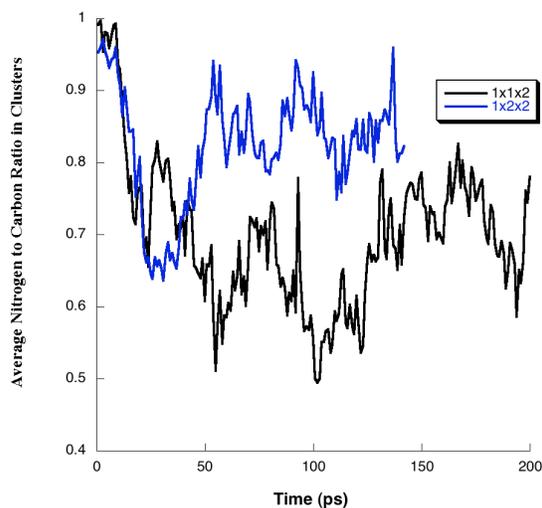


Fig. 7. Time evolution of the average nitrogen to carbon ratio in carbon-containing clusters obtained from simulated shocked TATB experiencing a shock wave speed of 10 km/s.

Finally, our MD simulations are providing very detailed decomposition mechanism for TATB. We have been able to construct a preliminary five-step decomposition mechanism for use in ALE3D grain scale simulations (e.g. micron-size pore collapse in TATB). The first step involves the decomposition of TATB into mono-furazan and water, followed by the formation of di-furazan and water. The third step accounts for the formation of high-nitrogen heterocycles and other gaseous products such as water, N₂, and CO from condensation reactions. The last two steps involve further decomposition of these heterocycles into N₂ and carbon clusters, and the final formation of graphite from these clusters. We obtained Arrhenius parameters for each mechanistic step from fit of rates at different temperatures, and found good agreement between Cheetah and our MD-based decomposition kinetics at these various T. We emphasize that refinement of this overall decomposition mechanism to a desired accuracy is always possible through inclusion of more detailed steps from our atomistic simulations.

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