SHOCK INDUCED DECOMPOSITION AND SENSITIVITY OF ENERGETIC MATERIALS BY REAXFF MOLECULAR DYNAMICS

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Abstract. We develop strain-driven compression-expansion technique using molecular dynamics (MD) with reactive force fields (ReaxFF) to study the impact sensitivity of energetic materials. It has been applied to simulation of 1,3,5-trinitrohexahydro-s-triazine (RDX) crystal subjected to high-rate compression typical at the detonation front. The obtained results show that at lower compression ratio $x = 1-V/V_0 < 40\%$ only a few of RDX molecules are decomposed, while for higher compressions ($x > 40\%$) all molecules decompose very quickly. We have observed both primary and secondary reactions during the decomposition process as well as production of various intermediates (NO_2, NO, $HONO$, OH) and final products (H_2O, N_2, CO, CO_2). The results of strain-driven compression-expansion modeling are in a good agreement with previous ReaxFF-MD shock simulations in RDX. Proposed approach might be useful for a quick test of sensitivity of energetic materials under conditions of high strain rate loading.

INTRODUCTION

Impact sensitivity of energetic materials (EM) is important property for the handling of explosive compounds. Determination, evaluation and prediction of impact sensitivity have stimulated numerous studies in last decades [5-13]. It has been found that the impact sensitivity is influenced by various molecular parameters such as the oxygen balance [14], the molecular electro-negativity [15-17], the lengths of the trigger bonds [18-20], and the charge distribution asymmetry around these bonds both in the ground [21-23] and in the excited states [24-27]. However, there is no comprehensive understanding of atomistic mechanisms governing the impact sensitivity and lack of computational techniques for its quick assessment.

In order to test and evaluate the sensitivity of pure explosive crystals, we introduce molecular dynamics (MD) approach equipped with the reactive force field (ReaxFF) capable to simulate the decomposition processes in energetic materials.

The ReaxFF is a reactive force field developed for various reactive systems. In this work we apply our approach to study the decomposition of RDX pure crystal and evaluate its sensitivity under conditions of very high-rate compression typical at the front of detonation wave. Such simulation studies can contribute to our understanding of the complex physicochemical processes that underlie the detonation of these materials and can led to methods for modifying the explosive or propellant formulations in order to obtain better performance and safety properties.

SIMULATION METHOD

We have developed strain-driven compression-expansion procedure coupled with MD simulations, as shown in Figure 1. It starts with a zero-pressure structure (initial cell volume: V_0) and includes four steps: (1) nonequilibrium MD with gradual step-by-step uniaxial compression of the simulation cell to a new volume $V=V_0(100-x)\%$ at
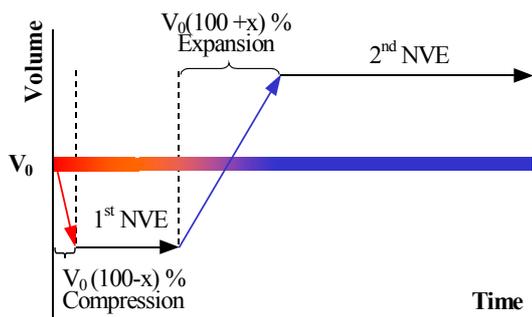
FIGURE 1. Four stages of strain-driven "compression-expansion" procedure to simulate high-rate deformation of energetic materials at the detonation front.

high compression rate (close to the detonation velocity), where $x=(V/V_0)*100\%$ is the volume compression ratio; (2) running 1-ps NVE MD simulation for a system in compressed cell; (3) nonequilibrium MD with step-by-step uniaxial expansion of the cell to $V = V_0 (100+x)\%$ backward in the compression direction at one third of the compression rate; (4) running 4-ps NVE MD simulation after the expansion. Here, we report the simulations in RDX crystal with six compression ratios x=30, 35, 38, 40, 42, and 45%. The compression rate is 8.76 km/s (which is close to the RDX detonation velocity).

The packing structure of RDX cell was taken from the Cambridge Structural Database (CSD). It has been minimized using the ReaxFF and then equilibrated at T=300 K for 5.0ps. To remove residual stresses, the NPT-MD has been performed at zero pressure for 2.5ps. The temperature of the system was controlled by Berendsen thermostat with damping constant of 50 fs. The final structure has been used to run the four-stages 'compression-expansion' procedure (see Fig. 1) to test the reactivity of RDX at different compression ratios. The integration time was 0.25 fs in the NVT and NPT equilibrium MD simulations, and 0.1 fs in the compression-expansion simulations. The bond order cutoff for molecule recognition used in the species analysis for all cases was set to 0.3.

RESULTS AND DISCUSSION

The results of are plotted in Figs. 2(a)-(c) for the system temperature, pressure, and total number of fragments per RDX molecule. It shows that the

degree of decomposition of RDX is changed dramatically above certain compression threshold.

For the lowest compression ratio x=30%, the system temperature always stays below 1200 K and the number of fragments per RDX molecule remains 1.0 during the simulation process except for a short period in the compression region. There the number of fragments becomes less than one because some of the molecules come very close to each other and form a pseudocluster which cannot be discriminated by recognition procedure using just a simple fixed bond-order cutoff criteria. The degree of such 'clusterization' increases when the compression ratio grows up in the beginning of the first simulation stage (see Figure 3b). However, some of the RDX molecules even at this stage are
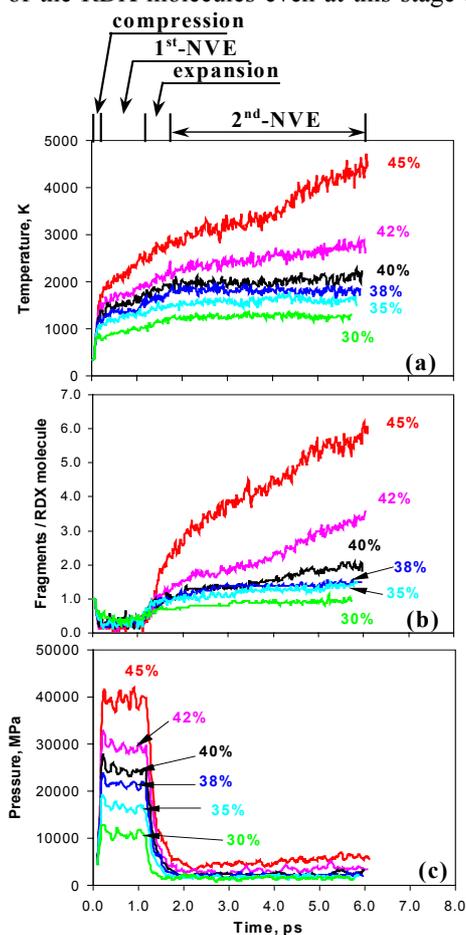

FIGURE 2. The RDX simulation results: (a) system temperature, (b) total number of fragments, and (c) pressure. Compression x=30, 35, 38, 40, 42, and 45%

get dissociated in simulations with x>40% while others remain highly strained under compression.

At highest compression ratio of x=45%, the system temperature increases dramatically up to 4520 K. Such sharp increase in the temperature is due to the initiation of chemical reactions in the system when chemical bonds break off under high temperature and pressure, and new products (H_2O, N_2, CO, and CO_2) are formed providing a positive energy balance. The number of fragments per molecule grows up to ~3.1 at the expansion stage with a further increase to 5.9 during the NVE stage.

In order to determine the critical compression ratio for initiation of the decomposition of RDX crystal, we measured the temperature and the total number of fragments at the end of each stage (i.e., compression, 1st-NVE, expansion, and 2nd-NVE). Figures 3(a) and 3(b) display the temperature and fragments vs. compression ratio at different stages. At lower compression ratios (x<40%), the temperature increases very little at all stages. It almost does not change at the end of expansion and 2nd-NVE stages, which correlates with a small change in the number of fragments (Figure 3b). However, the temperature and fragments increase dramatically when the compression ratio x>40%. For example, the final temperatures are 2790K and 4520K and the fragments per RDX molecule are 3.6 and 5.9 for x=42 and 45%, respectively. Our
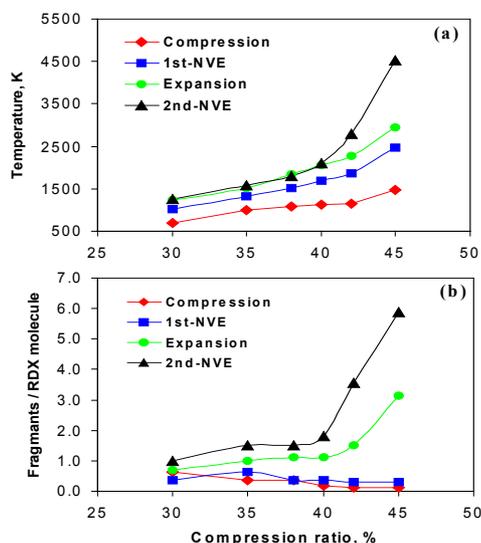

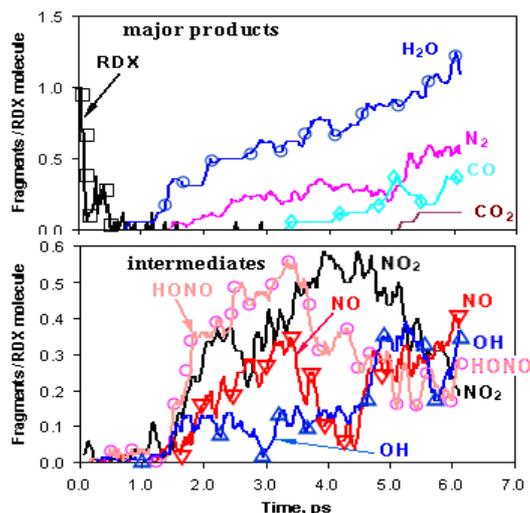**FIGURE 4.** A detail species analysis for the RDX crystal at the compression ratios of x=45%.

results suggest that the critical compression threshold could be ~40% for fast initiation of RDX at the compression rate of 8.76 km/s.

We also studied the evolution of the system pressure. At the compression stage, the pressure attains ~13 GPa for the lowest compression ratio x=30%, while it rises up to ~45 GPa for the highest ratio of 45%, overshooting the experimental value of 33.8Gpa [1]. For the threshold value of x=40%, the pressure at the end of compression remains about 25 GPa, and the number of fragments is

FIGURE 3. (a) Temperature and (b) fragments vs. compression ratio for RDX at different stages: compression, 1st-NVE, expansion, and 2nd-NVE.
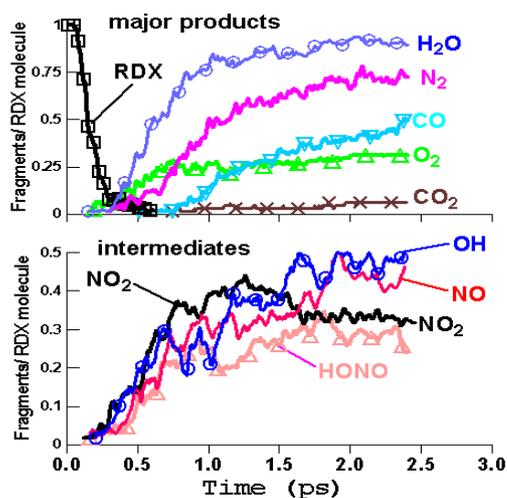

FIGURE 5. Product frequencies per molecule obtained from the piston-driven shock simulation in RDX cell with 64 RDX molecules at piston velocity u_p=5 km/s.

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slowly increasing up to 1.8 during the rest of simulation. Besides, the final pressure after the expansion remains relatively small in comparison to 4.4 and 6.4 GPa observed in the simulations with x=42 and 45%, correspondingly. Note that the pressure in the last two cases increases noticeably during the 2nd NVE stage (about 40 and 60%). It also indicates a critical change in the response of RDX crystal above the threshold of x=40%.

Figure 4 give a detailed analysis of evolution of major products and intermediates in the simulation with x=45%. The RDX molecules decompose very quickly producing such products as NO_2, NO, $HONO$, CO, CO_2, H_2O, N_2, OH, and O_2 in good qualitative agreement both with experiment [35] and our recent simulations of piston-driven shock compression of the RDX crystal (see Fig. 5).

In summary, we developed the ReaxFF-MD 'compression-expansion' modeling technique aimed to test reactivity of energetic materials under high strain rate conditions similar to those at the detonation front. The simulation results suggest that the ReaxFF can provide a computationally inexpensive tool to evaluate the reactivity and shock sensitivity of various energetic materials.

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