Shock Waves in High-Energy Materials: The Initial Chemical Events in Nitramine RDX

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We extend the reactive force field ReaxFF to describe the high energy nitramine RDX and use it with molecular dynamics (MD) to study its shock-induced chemistry. We studied shock propagation via nonequilibrium MD simulations at various collision velocities. We find that for high impact velocities (> 6 km/s) the RDX molecules decompose and react to form a variety of small molecules in very short time scales (< 3 ps). These products are consistent with those found experimentally at longer times. For lower velocities only NO_2 is formed, also in agreement with experiments.

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Recent advances in first principles modeling and experiments have led to enormous progress toward understanding complex gas-phase chemical phenomena. However, the progress in understanding the chemical processes in condensed phases has been considerably slower, particularly in processes as dynamical loading via shock waves important to understand the behavior of materials at extreme conditions and detonation of high energy (HE) materials. The coupling between shock loading, induced mechanical response, and complex chemistry makes the study of these materials very challenging with the result that there has been little progress in establishing a molecular level understanding. Most experimental and theoretical tools are not appropriate to characterize such heterogeneous and nonequilibrium systems subject to extreme mechanical conditions of pressure, temperature, and strain rates with length scales of nanometers, time scales of picoseconds, and involving a multitude of complex many-body chemical processes and intermediates. Consequently, despite its importance and important experimental advances (e.g., time resolved emission spectroscopy [1]), little is known regarding the coupling between the mechanical loading and detonation initiation in HE materials. Such a fundamental understanding is critical for the design of next-generation materials with improved performance and sensitivity.

Progress in understanding such processes requires following the detailed dynamics of reactions at a resolution in time and space that can be provided only by atomistic molecular dynamics. For example, Manaa *et al.* used quantum molecular dynamics to study the decomposition of six molecules of the nitramine HMX at high pressure and temperature [2]. Unfortunately, the large time scales (picoseconds) and length scales (nanometers) involved in shock waves make the direct use of *ab initio* quantum mechanical (QM) methods impractical. On the other hand, molecular dynamics (MD) simulations of model systems with simple chemistry have shown that atomistic modeling can provide valuable information regarding self-sustained detonation waves, role of defects on initiation, and desensitization [3–5]. Unfortunately, the empirical FFs used in molecular dynamics (MD) cannot describe the complex chemistry of real HE materials. In order to solve this problem, we developed a first principles reactive force field, ReaxFF [6], that accurately describes complex reactive processes while providing sufficient computational efficiency to allow the simulation of sufficiently large systems for sufficiently long times to examine shock-induced chemical processes. We report here the first MD simulations of shock-induced detonation initiation of the HE material RDX, cyclic-$[CH_2N(NO_2)]_3$, via high velocity impacts. Our simulations provide a full-physics, full-chemistry, first principles description of the initial chemical events induced by shock loading.

Key to our simulations is the reactive force field ReaxFF, which describes the energy and forces of a system in terms of [6]: (i) valence interactions based on the concept of partial bond order and determined *solely* from interatomic distances; this leads to proper description of bond breaking and formation processes; (ii) electrostatic interactions between all atoms using environment dependent charges calculated self-consistently at every step during the dynamics; (iii) shielded van der Waals interactions between all atoms. A key feature of ReaxFF is that all three terms described above are calculated between ALL atoms with every atom described using the same set of potential functions and parameters regardless of its environment. Thus, we do not specify that some pairs of atoms are bonded or part of a molecule.

In order to study nitramines, we extended the original hydrocarbon ReaxFF [6] to describe oxygen and nitrogen. The parameters of this extended ReaxFF are based on a large number of QM calculations (over 40 reactions and over 1600 equilibrated molecules) designed to characterize the atomic interactions under various environments [likely and unlikely (high energy)] an atom can encounter. The training set contains bond breaking and compression curves for all possible bonds, angle and torsion bending data for all possible cases as well as crystal data. The supplementary material [7] lists the data

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used to develop ReaxFF (not including the hydrocarbon training set described in [6]) and compares the accuracy of ReaxFF in fitting the QM data.

To illustrate the capability of ReaxFF in describing complex chemical reactions, Fig. 1 shows ReaxFF calculations (full lines with filled symbols) of the energetics of the 15 intermediate species and 15 transition states (see [8]) involved in the three most important pathways for unimolecular decomposition of RDX [sequential HONO elimination (circles), homolytic cleavage of an NN bond (NO_2 elimination) and subsequent decomposition (diamonds), and concerted decomposition (triangles)]. This is compared with the results from extensive *ab initio* QM calculations [8] (dashed lines with open symbols in Fig. 1) showing that ReaxFF describes accurately both the relative stability of the intermediate fragments and the transition states, providing an accurate description of the complex chemistry of RDX. ReaxFF also describes crystal data accurately; we obtain lattice parameters of $a = 13.7781$ Å, $b = 12.0300$ Å, and $c = 10.9609$ Å in good agreement with the experimental values (13.182 Å, 11.574 Å, and 10.709 Å) [9]. The calculated bulk modulus $B_T = 13.90$ GPa is also in good agreement with the experimental value (13.0 GPa) [10]. Both lattice parameters and bulk modulus were obtained by fitting Rose's equation of state [11] to energy-volume data obtained from isothermal, isochoric (constant N, V, and T) MD at $T = 300$ K (see supplementary material). The lattice parameters for the NVT simulations were obtained by homogeneously scaling those resulting from energy minimization (relaxing atomic positions and lattice parameters).

To simulate shock waves propagating in RDX, we considered the impact between two two-dimensionally periodic (infinite) slabs containing a total of 1344 atoms per unit cell. Each slab contains 32 RDX molecules forming a perfect crystal with cell parameters (experimental values) 11.574 Å × 10.709 Å × 52.72 Å. The slabs were thermalized at $T = 300$ K for 5 ps and then each atom is assigned the desired relative impact velocity ($+v_{\mathrm{imp}}/2$ and $-v_{\mathrm{imp}}/2$) on top of its thermal velocity. We then used constant energy MD to follow the time evolution of the system. This process produces two shock waves propagating into the slabs with particle velocity equal to half the impact velocity ($v_{\mathrm{part}} = v_{\mathrm{imp}}/2$). We report here the results for $v_{\mathrm{imp}} = 2, 4, 6, 8,$ and 10 km/s. Figure 2 shows that the shock velocity (v_{shock}) as a function of particle velocity (v_{part}) from our nonequilibrium MD simulations agrees well with the experimental unreactive shock Hugoniot from isothermal volume compression [12]. (Unreactive Hugoniot is used since the small size of our system does not allow a steady detonation.) The sound velocity obtained from the ReaxFF v_{shock} vs v_{part} curve is 2.93 nm/ps in excellent agreement with the experimental value of 2.78 nm/ps [12].

In order to follow the chemical processes as the shock wave propagates through the RDX slabs, we must define what we understand to be a molecule. Molecules are usually defined in *configuration* space (positions): When two atoms are closer than a given cutoff distance, they belong to the same molecule. However, under the extreme conditions of temperature and pressure found in shock waves, two atoms may be close in configurational space for times shorter than a vibrational period (if their c.m. kinetic energy is larger than the binding energy). Thus, we define two atoms as bonded if they are close in *phase* space (atomic positions and momenta); in practical terms we require the two atoms to have negative relative energy:

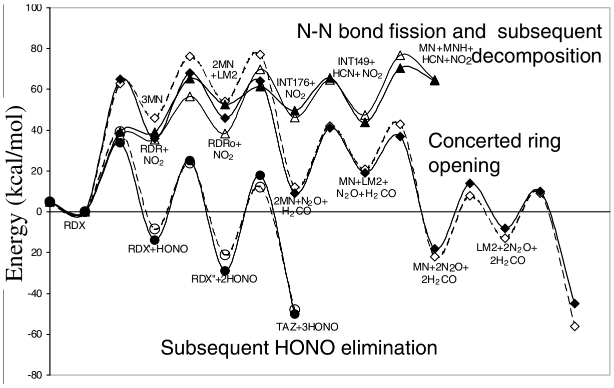

FIG. 1. Energetics of unimolecular decomposition mechanisms in RDX obtained using the ReaxFF (full lines with filled symbols) and with QM (dashed lines with open symbols) [8]. Circles represent the sequential HONO elimination, triangles show the decomposition process following homolytic N-N bond breaking (NO_2 elimination), and diamonds represent the concerted ring-opening pathway. Intermediates and products are described in [8].

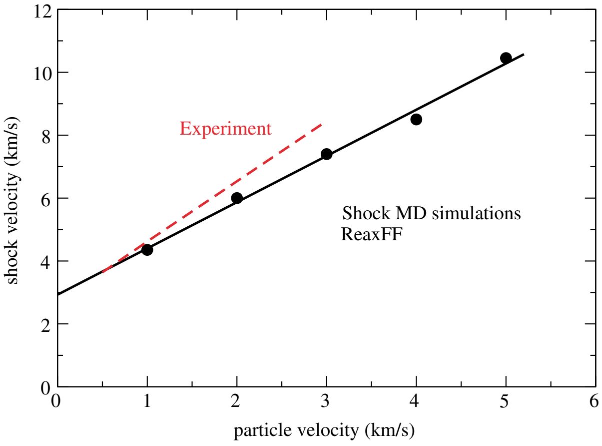

FIG. 2 (color online). The shock velocity (v_{shock}) as a function of particle velocity (v_{part}) obtained from nonequilibrium MD simulations using ReaxFF compared with the experimental (unreactive) results [12]. The sound velocity obtained from the ReaxFF results is 2.90 nm/ps, only 4.4% larger than experiment [12].

$$E_{ij} = V_{\text{int}}^{(ij)}(r_{ij}) + K_{\text{c.m.}}^{(ij)} < 0, \qquad (1)$$

where $V_{\text{int}}^{(ij)}(r_{ij})$ is the effective pairwise interaction between atoms i and j separated by a distance r_{ij} and $K_{\text{c.m.}}^{(ij)}$ is their c.m. kinetic energy. Since the interaction between two atoms depends strongly on their environment, we estimate $V_{\text{int}}^{(ij)}(r)$ using an effective two body interaction with a modified Morse term:

$$V_{\text{int}}^{(ij)}(r) = \begin{array}{ll} D_{ij}[\chi^2(r) - 2\chi(r)] & \text{if } r > R_{ij} \\ -D_{ij} & \text{if } r < R_{ij}, \end{array} \qquad (2)$$

where $\chi(r) = \exp[\gamma/2(1 - r/R_{ij})]$. In order to define unbiased parameters for Eq. (2), the energy of the effective interactions (D_{ij}) is proportional to the ReaxFF bond energy parameter [6] and the distances (R_{ij}) are proportional to the σ bond distances [6]. The three free parameters [energy scale, distance scale, and curvature (γ)] were chosen to correctly recognize RDX molecules in their crystalline form at $T = 300$ K. The prefactor used to define D_{ij} from bond energies is 1/3; this leads roughly to the energy of the σ bonds [6]. The distance parameters are obtained by multiplying the σ bond distances by 1.35; this leads to equilibrium bond distances. In order to avoid having different molecules in the compressed crystals appear to be clustered together, we chose a large value for the curvature $\gamma = 25$. Similar cluster recognition methods have been used in fragmentation [13].

Figure 3 shows the time evolution of the total population of various key molecules for $v_{\text{imp}} = 4$ to 10 km/s. For $v_{\text{imp}} = 4$ km/s, there is little chemistry, only ~30 NO_2 (~ 15% of the total) are formed during the course of the dynamics, some of these are just highly excited NN bonds that have a chance of appearing as broken in phase space. It is interesting to note that NO_2 is the only product in weak shocks even though the gas-phase energy barrier for HONO elimination is essentially the same (Fig. 1). This result is in agreement with photoelectron spectroscopy analysis on samples shocked with subdetonation strengths [14]. At $v_{\text{imp}} = 6$ km/s, a large number (~ 45) of NO_2 molecules are formed during the compression stage (up to ~1.2 ps). During the expansion stage another 15 NO_2 molecules form along with small quantities (~ 3) of OH, NO, and HONO. Around 1/3 of the original 64 RDX molecules remain intact after 4 ps. Increasing the impact velocity to $v_{\text{imp}} = 8$ km/s leads to a larger quantity (~ 60) of NO_2 molecules during compression (up to ~1 ps) but less (~ 10) in the expansion stage. Most notably, the production of N_2, OH, NO, and HONO increases significantly. At 8 km/s, we find significant production of both OH and NO at very early stages of the process (during compression). During the expansion stage, we find production of N_2 and HONO. At even higher impact velocity, $v_{\text{imp}} = 10$ km/s, the number of N_2 and OH increases significantly while the number of NO_2 decreases. In these simulations, the temperatures reach ~4000 K so that the asymptotic populations are

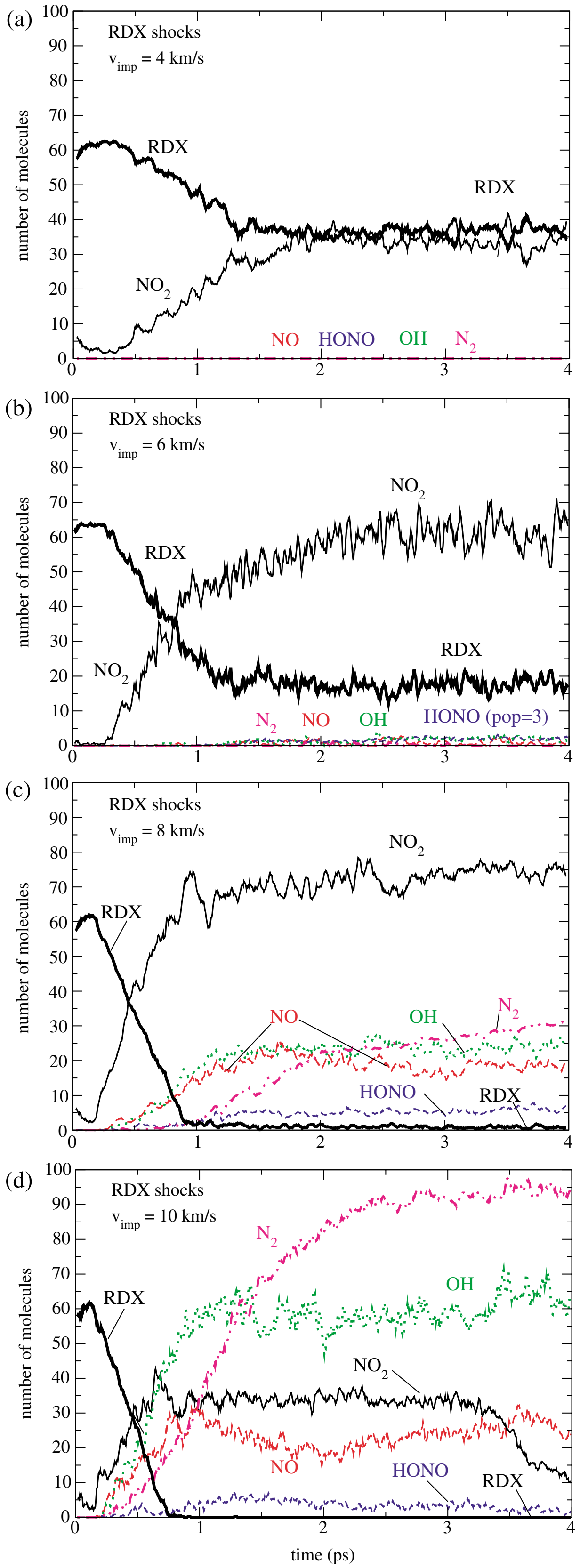

FIG. 3 (color). The time evolution of various fragments during the shock process for impact velocities: $v_{\text{imp}} = 4$ km/s (a); 6 km/s (b); 8 km/s (c); and 10 km/s (d). The initial number of RDX molecules is 64.

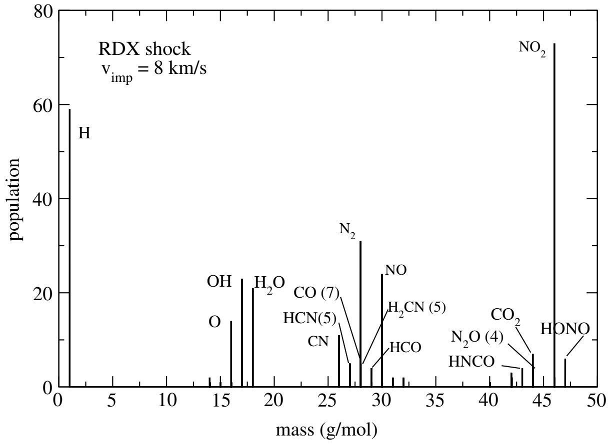

FIG. 4. Mass spectrum corresponding to $v_{\mathrm{imp}} = 8$ km/s at time $t = 4$ ps. Population as a function of mass for *all* the molecules found up to mass 50 g/mol (all species with population larger than 3 are labeled).

not in equilibrium and we expect subsequent reactions of these highly excited molecules.

A detailed analysis of the trajectories indicates complex (multimolecular) processes; for $v_{\mathrm{imp}} = 8$ km/s we find a large percentage of the final molecules (4 ps) were formed by multimolecular processes: 80% for HONO, 60% for OH, 20% for N_2, 10% for NO, and 5% for NO_2.

In addition to the species shown in Fig. 3, we find H, O, OH, H_2O, CN, HCN, CO, H_2CN, HNCO, N_2O, and CO_2; Fig. 4 shows the mass spectrum for $v_{\mathrm{imp}} = 8$ km/s at time $t = 4$ ps, showing *all* molecules found up to mass 50 g/mol (species with population larger than 3 are labeled).

In summary, we have developed the first principles ReaxFF that accurately describes the complex chemistry and mechanical properties of RDX. Nonequilibrium MD simulations using ReaxFF provide a detailed description of the chemical processes in the initial stages of shock detonation in condensed systems. These simulations allow us to elucidate such central issues in detonation theory as the following: Do bonds break promptly or is there a long induction time required to transform the translational energy of the shock into high-frequency bond vibrations that lead to chemistry? Our simulations show clearly that the primary reactions leading to NO_2, OH, NO, and N_2 occur at very early stages. We also find that although the barrier for the pathways leading to NO_2 and HONO is essentially the same, NO_2 is the main product for low shock velocities (< 6 km/s), in agreement with experiments [14]. As the impact velocity increases, N_2 and OH become the dominant product species at short times. Future work will target the characterization of processes with longer time scales reaching states closer to steady detonation condition.

This work demonstrates that first principles simulations of detonation can provide detailed information about the coupling between the mechanical load and the chemical response of HE materials. These relationships are critical to achieving an understanding of detonation initiation necessary to assess safety and sensitivity.

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