Quantum mechanical simulations of condensed-phase decomposition dynamics in molten RDX

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Abstract. A reaction rate model of condensed-phase decomposition hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) under pressures up to several GPa is needed to support mesoscale simulations of the energetic material’s response to thermal and shock loading. A prerequisite to developing such a model is the identification of the chemical pathways that control the rate of initial dissociation and subsequent decomposition of molecular fragments. Presented here are density functional theory based molecular dynamics simulations of reactive dynamics in molten RDX at an initial temperature of 1500 K and different values of the melt density chosen to probe the effect of hydrostatic compression. The observed dissociation mechanisms and the effect of pressure on the corresponding rate constants are discussed.

1. Introduction
The sensitivity of energetic compositions for solid propellants and high explosives is known to be strongly affected by the ingredient microstructure. Computational methods that can model local fluctuations of temperature and stress at microstructural heterogeneities and link them to the onset of chemical reactions are needed to rationalize the effect of the microstructure on the material’s sensitivity. Several such methods are currently being pursued, ranging from the hydrodynamic simulations of composite materials [1–3] and granular flow [4] to the particle-based simulations of imperfect molecular crystals [5, 6]. Thermochemical models that describe the relevant chemical reactions and the resulting release of chemical energy are needed to support these developments.

The chemical energy release in energetic solids such as RDX is driven by a multitude of elementary chemical reactions, which are responsible for molecular decomposition and combustion of molecular fragments [7]. The rates and exothermicity of these reactions steeply rise as chemistry proceeds. The finite rates of heat and mass transport result in a rapidly increasing temperature and pressure behind the reaction front. Understanding of the reaction mechanisms in RDX under a wide range of temperatures and pressures is necessary to develop a thermochemical model that captures the variations in the energy release rate during the formation of the reaction front.

Quantitative kinetic data on condensed-phase RDX decomposition under high temperatures and pressures is scarce. Global reaction pathways below 700 K are known from the thermogravimetric measurements [8, 9] and the corresponding rates have been estimated from the measured speciation profiles [10]. However, the observed global pathways are known to result from complex manifolds of elementary reactions [11] and may be altered by higher temperatures.
The elementary reactions of gas-phase RDX decomposition are known from quantum-mechanical calculations [12–14]. The theoretical rate constants have been tested in modeling flame chemistry above a burning strand of RDX-based propellants [15–17]. Still discrepancies remain between the gas-phase model predictions and the observed condensed-phase reaction intermediates [18]. A recent study on bimolecular reactions has provided a further step toward reconciling the gas-phase mechanisms and the condensed-phase measurements [18]. If a correspondence between the observed condensed-phase mechanisms and the gas-phase elementary reactions is established, it can serve as a basis for extrapolating the measured condensed-phase kinetics to higher temperatures.

High pressures may further affect the condensed-phase kinetics and compete with high temperatures in promoting some elementary reactions and suppressing others [19]. Radical pathways dominating gas-phase RDX decomposition [12, 14] are known to be suppressed by high pressures [20, 21]. One experimental study reported a full suppression of homolytic fission of N-N bonds in solvated RDX already at 0.1 GPa [22]. High pressures may thus cause a transition from the initial N-N fission and the resulting secondary reactions [12, 14] to a chain of concerted eliminations [21, 23], thus altering the global decomposition kinetics.

Quantum-mechanical simulations that can probe the reaction mechanisms directly in crystalline and molten RDX are needed to delineate the effect of the condensed phase and high pressures on decomposition kinetics. Presented here are ab initio molecular dynamics (MD) simulations of the initial decomposition reactions in molten RDX under GPa pressures. Density functional theory (DFT) within the generalized gradient approximation and periodic boundary conditions were used to compute the electronic energy and gradients necessary to propagate the classical MD trajectories. The details of these calculations are given in section 2. The computed trajectories were analyzed to identify which bonds were broken. These numerical results are discussed in section 3. A summary is given in section 4.

2. Computational method
Cubic periodic cells with 8 RDX molecules were used to model the disordered, liquid-like, environment of molten RDX. The cell volumes were chosen to sample 4 different densities of the melt—1.47, 1.63, 1.96, and 2.12 g/cm³—and kept fixed in the MD simulations. A total of 40 sets of the initial coordinates (10 sets per density value) were generated by placing 8 RDX molecules at their gas-phase DFT equilibrium geometries in periodic cells and then scaling the cell to one of the four volumes. Each configuration was initially equilibrated at 500 K using 100 ps long canonical (NVT) MD runs based on the Smith-Bharadwaj (SB) potential [24]. The equilibrated atomic velocities were scaled to the target temperature of 1500 K and equilibrated again at 1500 K using 0.5 ps long NVT MD runs. The resulting atomic coordinates and velocities were propagated in 10 ps long microcanonical (NVE) DFT MD runs that sampled the decomposition dynamics. The canonical SB and DFT MD simulations used the Nose-Hoover integrator [25] with a 0.5 fs time step. The microcanonical DFT MD simulations used a predictor-corrector integrator [26] with a 0.5 fs time step. The SB calculations were done with the LAMMPS code [27] and the DFT calculation with the CP2K code [28].

The DFT MD simulations used the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [29]. A double-zeta set of Gaussian-type atomic orbitals was used for the valence Kohn-Sham (KS) orbitals, a set of plane waves truncated at 6800 eV for the valence KS density, and an ultrasoft pseudopotential [30] for the core density. Sampling of the Brillouin zone was restricted to the Γ point.

The spin-unrestricted DFT variant is typically required to describe the singlet biradical transition state to homolytic fission [31]. In the current simulations, it was found that converging the spin-unrestricted equations to the correct symmetry broken orbitals is challenging when multiple bonds were broken. Instead, a new spin-restricted DFT variant was used, wherein the
frontier KS orbitals were kept fractionally occupied using the Fermi “smearing” function [32] with a fixed width, $\sigma_F = 0.27$ eV. The width was chosen based on the computed differences between such “restricted smeared” and unrestricted, symmetry-broken PBE energies in single-molecule calculations. The resulting “restricted smeared” DFT energies were found to be within 2.5 kcal/mol of the unrestricted, symmetry-broken energies along the entire minimal-energy path (MEP) to fission, including the limit of the separated radical fragments. In comparison, the spin-restricted DFT energies without smearing are $\sim 25$ kcal/mol too high in this limit. The “restricted smeared” DFT variant appears to be useful in other DFT simulations of condensed-phase reacting systems and will be discussed in detail elsewhere.

3. Results
Overall, 40 MD trajectories were computed, each sampling the initial temperature of 1500 K and one of the four densities of the melt. During the 0.5 ps NVT equilibration runs, the average MD pressures ranged from $\sim 1$ GPa for the lowest simulated density to $\sim 10$ GPa for the highest density. However, the fluctuations in the instantaneous MD pressures were very large, on the scale of 1 GPa. Such large fluctuations were attributed to the small periodic cells used to model the disordered environment of the melt. Ongoing simulations with 27 RDX molecules per periodic cell have indicated that the three-fold increase in the system size can result in as much as a ten-fold decrease in the pressure fluctuations.

Molecular structures extracted from one representative trajectory are shown in figure 1. In this trajectory, fission of an N-N bond was first observed at the simulated time of 1.84 ps leading to the loss of an NO$_2$ radical. At 2.48 ps and at 4.50 ps two more N-N bonds and C-H bond were found broken leading to two more NO$_2$ radicals and one HONO moiety. At 5.38 ps, a recombination between an NO$_2$ radical and one of the radical fragments of RDX was observed leading to the recovery of an RDX molecule. Finally, at 7.10 ps more N-N fission events were observed, but also dissociation of HONO into OH and NO radicals.
Figure 2. (a) Observed rates of bond breaking in molten RDX at an initial temperature of 1500 K and four densities of the melt. Shown are the fractions of unreacted RDX molecules totaled over a set of 10 trajectories for the melt density of 1.47 (blue circles), 1.63 (green diamonds), 1.96 (orange crosses), and 2.12 g/cm$^3$ (red triangles) together with the corresponding exponential fits (solid lines). (b) The branching ratios between the two types of broken bonds that led to the observed rate reported in panel (a). Shown are the total numbers of broken N-N (blue filled) and C-H (red empty) bonds for sets of 10 trajectories per density value.

To analyze the computed trajectories, the atomic coordinates describing each RDX molecule were extracted at a 0.1 ps interval and the intramolecular N-N, C-H, and C-N bond lengths were calculated. The calculated bond lengths as functions of the simulated time were compared to the bond distances in the corresponding gas-phase transition structures [13]: 3.2 Å for N-N, 2.0 Å for C-H, and 2.6 Å for C-N. If a bond distance was found to exceed one of these values, the RDX molecule was considered dissociated at that moment and not further analyzed. The observed numbers of dissociated RDX molecules totaled over 10 trajectories per melt density are shown as functions of time in figure 2(a). If each reactive event was independent of the others, then the number of unreacted molecules should decay exponentially with the rate equal to the total rate of all elementary mechanisms [33]. Single-exponential fits to the observed fractions of unreacted RDX molecules in 10 trajectories for each density value are also shown in figure 2(a).

The branching ratios between the types of broken bonds that lead to the observed molecular dissociation are shown in figure 2(b). At the lowest simulated density, 1.47 g/cm$^3$, about three times as many molecules dissociated via breaking of a N-N bond as via breaking of a C-H bond. No instances of breaking a C-N bond was observed. The number of molecules dissociated via breaking of a N-N bond rapidly decreased with the increased density: from 47 at the lowest density to 7 at the highest density. In contrast, the number of molecules dissociated via breaking of a C-H bond decreased only slightly: from 16 at the lowest density to 11 at the highest density. A slight increase from 8 broken C-H bonds at 1.96 g/cm$^3$ to 11 at 2.12 g/cm$^3$ indicates that the observed changes in the number of broken C-H bonds may be due to a statistical variation. Note that the bond lengths analysis used here did not differentiate between bond breaking due to intramolecular thermal motion (a unimolecular reaction) or due to an intermolecular atom transfer (a bimolecular reaction). Correspondingly, the observed instances of broken C-H bonds can indicate either a unimolecular elimination or a bimolecular H-atom transfer.

The observed rates and the branching ratios reported in figure 2 are qualitatively consistent with the known effect of higher pressures on homolysis. However, even at the highest simulated density, which corresponded to an estimated pressure of 10 GPa, N-N homolysis accounted for nearly half of the observed broken bonds. In contrast, the experimental measurement [22] reported a full suppression of homolysis at 0.1 GPa. Further investigations are need to pinpoint the origin of this difference. As mentioned above, finite size effects led to the large fluctuations...
in the instantaneous observed MD pressures. Simulations with larger unit cells are currently underway to evaluate these effects. Also, previous simulations [34] indicated that an NO$_2$ radical produced via N-N fission can abstract an H atom from the RDX fragment or a neighboring molecule. If such a secondary reaction is facile, homolysis and elimination can result in similar reaction intermediates, making experimental identification challenging. The simulations with larger units cells should provide a better sampling of such secondary reactions. Finally, the effect of pressure on the rate of homolysis can be diminished by higher temperatures. The current simulations sampled the initial temperature of 1500 K, while the measurements [22, 23] were done at a significantly lower temperature, 500 K. The minimal-energy path for molten-phase fission and elimination are currently being computed to allow condensed-phase transition state theory calculations of the rate constants for a wide range of temperatures.

4. Summary
DFT-based MD simulations were used to study the initial reactions in molten RDX under a high temperature and high pressures. Eight RDX molecules in periodic cells of four different volumes were used to model the disordered environment of the melt under hydrostatic compression. Forty MD trajectories were computed for an initial temperature of 1500 K and the melt densities varying from 1.47 to 2.12 g/cm$^3$ to sample the reaction dynamics. Breaking of N-N bonds was found to account for most dissociation at the lowest density, but the total number of broken N-N bonds decreased for larger densities. Breaking of C-H bonds accounted for the remaining reactive events and the total number of broken C-H bonds remained approximately the same for all the densities. These observations are qualitatively consistent with the known effect of pressure on homolysis and concerted elimination [20, 21]. However, even at the highest density, which corresponded to an estimated pressure of 10 GPa, homolysis accounted for nearly a half of reactive events. In contrast, an experimental study reported a full suppression of homolysis at 0.1 GPa [22]. Larger simulations with 27 RDX molecules per periodic cell are currently underway to estimate the finite size effects and to investigate the secondary mechanisms. Condensed-phase transition state theory calculations are also being pursued to delineate the effects of temperature and pressure on the rate constants.

Acknowledgments
This work was supported by the Office of Naval Research, both directly and through the Naval Research Laboratory, and by the Department of Defense High Performance Computing Modernization Program Software Application Institute for Multiscale Reactive Modeling of Insensitive Munitions.

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