Multistage reaction pathways in detonating high explosives
Ying Li, Rajiv K. Kalia, Aiichiro Nakano, Ken-ichi Nomura, and Priya Vashishta

Citation: Applied Physics Letters 105, 204103 (2014); doi: 10.1063/1.4902128
View online: http://dx.doi.org/10.1063/1.4902128
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/105/20?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Initial chemical events in shocked octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine: A new initiation decomposition mechanism

Combining ab initio quantum mechanics with a dipole-field model to describe acid dissociation reactions in water: First-principles free energy and entropy calculations

Modeling deflagration-to-detonation transition in granular explosive pentaerythritol tetranitrate

Simulated thermal decomposition and detonation of nitrogen cubane by molecular dynamics

Interplay of explosive thermal reaction dynamics and structural confinement
Multistage reaction pathways in detonating high explosives

Ying Li,1,2 Rajiv K. Kalia,1 Aiichiro Nakano,1 Ken-ichi Nomura,1 and Priya Vashishta1
1Collaboratory for Advanced Computing and Simulations, Department of Physics and Astronomy, Department of Computer Science, and Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California 90089-0242, USA
2Argonne Leadership Computing Facility, Argonne National Laboratory, Argonne, Illinois 60439, USA

(Received 6 October 2014; accepted 3 November 2014; published online 19 November 2014)

Atomistic mechanisms underlying the reaction time and intermediate reaction products of detonating high explosives far from equilibrium have been elusive. This is because detonation is one of the hardest multiscale physics problems, in which diverse length and time scales play important roles. Here, large spatiotemporal-scale reactive molecular dynamics simulations validated by quantum molecular dynamics simulations reveal a two-stage reaction mechanism during the detonation of cyclotrimethylenetrinitramine crystal. Rapid production of N2 and H2O within ~10 ps is followed by delayed production of CO molecules beyond ns. We found that further decomposition towards the final products is inhibited by the formation of large metastable carbon- and oxygen-rich clusters with fractal geometry. In addition, we found distinct unimolecular and intermolecular reaction pathways, respectively, for the rapid N2 and H2O productions.

© 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4902128]
porous), and these heterogeneities lead to complex multidimensional flows even in macroscopically unidirectional detonation. In particular, voids cause localized hot spots, which essentially drive the decomposition reaction. To mimic this effect, a void of size $3 \times 3 \times 3$ unit cells is randomly inserted in every $5 \times 5 \times 6$ unit cells of the RDX crystal. Figures 1(a) and 1(b) show the atomic structure of an RDX molecule and the configuration of the RDX crystalline unit cell, respectively. The number of RDX molecules inside the system is $27 \times 552$, amounting to the total number of atoms to be $578\,592$.

Starting from this initial configuration, we perform MD simulations with a time step of 0.1 fs up to 70 ps. Figure 1(c) shows a schematic diagram of shock loading. To model the shock wave and subsequent detonation and expansion, we employ a planar impact loading by a rigid-wall piston with the speed of $v_p = 6 \text{ km/s}$ from the right end onto the system. When the shock front hits the rigid wall at the left end of the simulation box, it is reflected back to the right. It takes about 11 ps for the shock wave to travel for a distance of 110 nm, indicating the shock speed of $\sim 10\text{ km/s}$. This is above the RDX detonation speed of 8.75 km/s, suggesting an overdriven detonation. After the shock front bounces back towards right, the piston is removed to allow the detonated RDX to expand freely. The expansion continues until the volume of the system becomes three times the original value. Figure 1(d) shows a colored map of temperature as a function of the $x$ position and time. The initial length of RDX is $X_0 = 222.8 \text{ nm}$. The highest temperature of the system reaches 3000 K near the shock front (shown as diamond-shaped red spots in Fig. 1(d)) before 20 ps, and during compression at 20–30 ps. A similar colored map for pressure distribution is shown in Fig. S1 in the supplementary material.

To study the chemical reaction pathways, we have performed fragment analysis, where a cluster of covalently bonded atoms is counted as a molecule. Here, a pair of atoms are considered connected if the bond order of the pair is greater than 0.3 (Ref. 41) and their distance is less than a critical value slightly larger than the corresponding covalent bond length. Figure 2 shows the number of molecular products as a function of time. These include the final products ($\text{H}_2\text{O}$, $\text{N}_2$, and $\text{CO}$) of the overall reaction of RDX decomposition

$$\text{C}_3\text{H}_6\text{N}_6\text{O}_6 \rightarrow 3\text{H}_2\text{O} + 3\text{N}_2 + 3\text{CO}. \quad (1)$$

Among the final products, we observe rapid production of $\text{N}_2$ and $\text{H}_2\text{O}$ during the initial expansion phase followed by plateaux in the later stage. We also observe a very slow production of CO. To estimate the time constant $\tau_a$ for the production of the $a$-th final product ($a = \text{H}_2\text{O}, \text{N}_2, \text{CO}$), we fit the yield of the corresponding molecular fragments as a function of time as

$$\eta_a(t) = 1 - \exp(-t/\tau_a). \quad (2)$$

Here, $\eta_a(t)$ is defined as the ratio of the observed number of the $a$-th fragments at time $t$ to the asymptotic number for $t \to \infty$ expected from Eq. (1) (The detailed procedures for estimating the time constants and associated error bars are described in the supplemental material.40). The fitting produces $\tau_{\text{H}_2\text{O}} = 10 \pm 2$ ps, $\tau_{\text{N}_2} = 30 \pm 4$ ps, and $\tau_{\text{CO}} = 900 \pm 400$ ps. Namely, the detonation reaction occurs in two stages: Rapid production of $\text{N}_2$ and $\text{H}_2\text{O}$, followed by much slower production of CO. The rapid production of $\text{N}_2$ and $\text{H}_2\text{O}$ at an early stage of detonation is consistent with earlier simulation by Strachan et al. In their simulation for 5 ps, the dominant products were $\text{N}_2$ and $\text{H}_2\text{O}$. Also, slightly different multistage reactions were observed experimentally by Anisichkin for a related HE, RDX/TNT mixture, using an isotope tracer method. In order to verify that the two-stage reaction is not an artifact of the simulation schedule, we have performed another simulation using a different schedule. Figure S2 shows the number of molecular fragments as a function of time for the

![FIG. 1. (a) RDX molecule, where gray, cyan, blue, and red spheres represent C, H, N and O atoms, respectively. (b) RDX unit cell. The 8-molecule (or 168-atom) unit cell has the lattice parameters of $a = 13.182 \text{ Å}, b = 11.574 \text{ Å}, c = 10.709 \text{ Å}$, and $\alpha = \beta = \gamma = 90^\circ$. (c) Schematic diagram of shock-induced detonation and propagation in the [100] crystallographic direction. (d) Colored map of temperature as a function of the $x$ position and time.](image)

![FIG. 2. Number of molecular fragments as a function of time. As the shock front begins to reflect, a rapid production of $\text{H}_2\text{O}$, $\text{OH}$, and $\text{N}_2$ is observed. Shortly after the expansion phase begins, various chemical products such as $\text{CO}$, $\text{CO}_2$, and NO are produced.](image)
alternative simulation, which also exhibits two distinct reaction rates.\textsuperscript{40} In addition, we have performed another simulation, in which the original schedule was applied to another HE, triaminitritobenzene ($C_{6}H_{2}O_{3}N_{6}$ or TATB). For TATB, we have not observed a separation of time scales. These results indicate that the two-stage reaction is an intrinsic property of RDX.

In order to identify the reaction pathways for the rapid production of $N_{2}$ and $H_{2}O$, we backtrack where the atoms composing individual $N_{2}$ and $H_{2}O$ molecules originate in the initial configuration of the simulation. For some of the $N_{2}$ and $H_{2}O$ products, all the atoms that constitute a molecule originate from a single RDX molecule, i.e., unimolecular pathways. For others, atoms from different RDX molecules form $N_{2}$ and $H_{2}O$ molecules, i.e., intermolecular pathways. Examples are shown in Fig. 3, where the $H$, $O$, and $N$ atoms that constitute the circled $N_{2}$ and $H_{2}O$ products in Fig. 3(b) are highlighted, respectively, with green, yellow, and magenta colors in the initial configuration in Fig. 3(a). In Fig. 3(a), one green $H$ atom belongs to a $–CH_{2}$ group of one RDX molecule, while another green $H$ atom belongs to a $–CH_{2}$ group of another RDX molecule and one yellow $O$ atom belongs to an $–NO_{2}$ group of the latter RDX molecule. Immediately after the reversed shock front traveling rightward passes, cleavages of $C$ and $H$ atoms from $–CH_{2}$ groups and $N$ and $O$ atoms from $–NO_{2}$ group release the highlighted $H$ and $O$ atoms, which together form the $H_{2}O$ molecule circled in Fig. 3(b), signifying an intermolecular pathway. In contrast, for the $N_{2}$ molecule circled in Fig. 3(b), both magenta $N$ atoms composing the $N-N$ bond originate from one RDX molecule in the initial configuration in Fig. 3(a), i.e., a unimolecular pathway. We have examined the origin of the other $N_{2}$ molecules as well, as shown in Fig. S3.\textsuperscript{40} Interestingly, most of them are from $N-N$ bonds within single RDX molecules, even though $–NO_{2}$ functional groups cleave first when the shock front passes RDX, as was seen in a previous simulation.\textsuperscript{15} Experimental results also indicate that $NO_{2}$ is a direct product of $N-N$ hemolysis in the initial reaction stage under shock.\textsuperscript{44}

To better identify the source of the most abundant fragments ($N_{2}$ and $H_{2}O$), Fig. 3(c) plots the fraction of $N_{2}$ and $H_{2}O$ molecules that are produced by unimolecular pathways, i.e., all constituent atoms of each molecule originate from a single RDX molecule in the initial configuration: $f_{\text{intra}}^{i}$ ($\alpha = N_{2}, H_{2}O$). We see that $N_{2}$ production mechanism is predominantly unimolecular. Namely, 75% of the $N_{2}$ products are from $N-N$ bonds within single RDXs. In contrast, only 15% of $H_{2}O$ products are formed by $H$ and $O$ atoms from single RDXs, i.e., $H_{2}O$ production mechanism is intermolecular. Figure S4 provides detailed analysis of the origin of the $H$ and $O$ atom of $H_{2}O$.\textsuperscript{40} This implies that $N$ atoms react locally, while $H$ and $O$ atoms move more actively to react with those from further non-adjacent RDX molecules. This is consistent with simulation results by Wu et al.,\textsuperscript{2} who found a catalytic behavior of water in the detonation of HE. They found that $H_{2}O$ actively participates in reactions by transporting oxygen between different fragments, instead of being a mere stable final product. The role of hydrogen as long-ranged reaction participants is understandable because of its lightest mass. Accordingly, $H$ atoms can travel farther to bond with $O$ atoms from other reactant molecules to form $H_{2}O$.

To understand the reaction pathways involving the rest of the elements (particularly carbon) and the reason behind the slow production of CO molecules, we study the time evolution of the population of large clusters remained in the system. Here, we define a large cluster as that containing more number of atoms than the 21-atom RDX molecule. Figure 4(a) shows the fraction $N_{C}/N_{T}$ of the number of atoms in larger clusters, $N_{C} = \sum_{i=1}^{C} C(i)i$, vs. the total number of atoms in the system, $N_{T} = \sum_{i=1}^{T} C(i)i$, as a function of time. Here, $C(i)$ is the number of molecular fragments each consisting of $i$ atoms. In the compression phase, the number of coagulated atoms, which are from the compressed part of RDX, increases linearly with time. Once no further shock loading is applied on the system, the large clusters start to decompose. Especially in the initial expansion phase, the sudden release from the right opening side leads to massive decomposition of the large clusters, which produce vast amount of small fragments such as $N_{2}$ and $H_{2}O$. However, in the later stage, lower temperature and density cannot sustain further chemical decomposition reactions. As a result, more than 10% of the atoms remain in large clusters even at the end of the total simulated time of 70 ps. The characteristic decay time of the large clusters is estimated by the exponential fitting as $\tau_{\text{decay}} = 800 \pm 500$ ps, which is close to the reaction time of CO: $\tau_{\text{CO}} = 900 \pm 400$ ps. Therefore, we can identify the large metastable clusters to be the major retardant of the CO-production reaction. Figure S5 provides more detailed analysis of the large clusters.\textsuperscript{46}
This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.125.4.86

We next perform stoichiometric analysis of the large clusters. Figure 4(b) shows the averaged atomic compositions, \( c(x) \) (where \( x = C, H, O, N \)), of the large clusters as a function of time, which is normalized as \( \Sigma c(x) = 1 \). In the figure, the dashed lines show the composition for different elements in the RDX molecule: \( c_0(C) = 3/21 \) while \( c_0(H) = c_0(O) = c_0(N) = 6/21 \). Comparison of the compositions \( c(x) \) of the large clusters with those of the RDX reactant \( c_0(x) \) shows that the large clusters at the end of the simulation are not only carbon-rich but also oxygen-rich. Namely, the average stoichiometry of the large clusters at 70 ps is summarized as \( \text{C}_{4.94}\text{H}_{4.76}\text{O}_{6.99}\text{N}_{4.31} \) (where the numbers are normalized to add up to 21—the number of atoms in an RDX molecule), which contains more C and O atoms than the RDX reactant, \( \text{C}_3\text{H}_6\text{O}_6\text{N}_6 \). Since these large C- and O-rich clusters remain metastable, it inhibits the formation of final CO products.

This mechanism of large C- and O-rich clusters as reaction retardants is akin to a recently proposed mechanism in Ref. 46. The generalized gradient approximation \( 47 \) is used for the exchange-correlation energy. The plan-wave cutoff energy is set as 400 eV. Within the time period of the QMD simulation, the selected fragment remains stable (see the movie S1 in supplementary material \( 46 \)).

In summary, our ReaxFF-MD simulations clearly revealed two time scales for the formation of final products of RDX during detonation. First, \( \text{N}_2 \) and \( \text{H}_2\text{O} \) (and \( \text{OH} \)) are formed rapidly within \( \sim 10 \) ps, resulting from uni- and intermolecular reaction pathways, respectively. Subsequently, CO starts to form at a very low rate (i.e., the reaction time \( \sim 1 \) ns). We found that the CO production is retarded by the formation of large C-rich and O-rich clusters. Such atomistic understanding of the reaction time and intermediate products provides valuable insight into broad technologies involving HEs. An example is rational design of insensitive energetic materials and detonation synthesis of materials such as nanodiamond. \( 3 \)

This work was supported by the Office of Naval Research Grant No. N00014-12-1-0555.