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Thermal decomposition behaviour of RDX by first-principles molecular dynamics simulation

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Thermal decomposition behaviour of cyclotrimethylenetrinitramine crystal (with a density of 1.81 g/cm³ and at a temperature of 3000 K) was simulated using density functional molecular dynamics up to 33 ps. During the entire simulation time, the major products are N₂, H₂O and CO₂; and their populations generally increase with time. In the initial stage of decomposition, we observed formation of NO₂ groups carrying about one positive charge, which might play some roles in the further decomposition process. The energy transformation during the thermal decomposition process is also discussed.

Keywords: thermal decomposition; molecular dynamics; RDX; density functional theory

1. Introduction

Energetic materials, which release a large amount of heat during detonation and deflagration, have wide applications in both military and commercial fields [1]. Understanding the decomposition behaviour and the reaction mechanisms of thermal decomposition of energetic materials are important for designing more efficient and safer high explosives. Cyclotrimethylenetrinitramine (RDX, C₃H₆N₆O₆) is considered as one of most important high explosives and monopropellants. In previous works, optical spectra [2–5], shock sensitivity [6], decomposition mechanism [7–16] and high-pressure behaviour [17,18] of RDX crystal have been investigated by different groups.

Among those studies, particular attention has been paid to the thermal decomposition mechanism of RDX, and several possible initial reaction pathways in the condensed phase of RDX have been proposed [7,11,13,19–22]. Among these pathways, the most probably initial step is the dissociation of the N–NO₂ bond [7,11,13,20,21], which was evidenced by Wight and Botcher [11,20]. Another possible initial process of concerted ring fission was also suggested [7,13,22]. In addition, the N–NO₂ bond rupture mechanism was reported by Melius [23] for gas-phase octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) molecule and Lewis et al. [24] for α -HMX polymorph.

In recent years, reactive force field (ReaxFF) [25] has been introduced to describe the complex reactive process in organic chemical reaction. For the energetic materials, Strachan et al. [26] developed the ReaxFF parameters for nitramine and simulated the NVT

(constant N, V, and T) decomposition of shocked RDX at $T = 300$ K, with periodic boundary condition at various collision velocities. They found that the populations of main products alter with different shock-wave velocities and that NO₂ is the dominant product with low velocity. With high velocity, N₂, OH, NO and NO₂ were the major final molecules (usually referring to neutral specimens), small groups (charged molecules/ions with well-defined formula) or molecular fragments (direct fragments of the original RDX molecules without well-defined chemical formula), while H, O, CN, HCN, CO, H₂CN, HNCO, N₂O and CO₂ were also found. Later, the same group [14] employed the ReaxFF-based molecular dynamic (MD) to simulate the initial chemical decomposition process of RDX at three densities and three temperatures. From both studies, the formation of NO₂ was dominant reaction at the initial stage; while in a recent study [14] NO₂ was only the intermediate product instead of the final one. Besides, Gump and Peiris [8] used the ReaxFF MDs to study the thermal decomposition of RDX at different compression ratios and to discuss the pressure effect. They argued that RDX will decompose rapidly at high pressure with increasing temperature. They also employed ReaxFF–MD to simulate the impact sensitivity of RDX and the results were consistent with earlier shock-wave simulation of RDX [26].

Even though the ReaxFF was elaborately developed to reproduce the quantum mechanical results, it was usually fitted to the *ab initio* or experimental data of molecules/solids under normal conditions (like atmospheric pressure and room temperature [25]). Thus, it is still questionable

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whether it remains valid in the simulation of extreme conditions of high temperature and/or high pressure. In order to go beyond empirical simulations and to gain more insight into the thermal decomposition behaviour of RDX, we carried out MD study using density functional theory (DFT) to simulate the decomposition dynamics of RDX crystal at a high temperature of 3000 K.

2. Computational methods

The decomposition behaviour of RDX at a high temperature of 3000 K was simulated by DFT-based MD approach implemented in a DMol program [27]. We adopted the local density approximation for exchange–correlation interaction and the double numeric basis sets [27]. Instead of solving the Schrödinger equation with standard self-consistent field (SCF) approach, we used a non-SCF Harris [28] functional approximation to speed up the electronic structure calculation at each MD step. The Brillouin zone of the reciprocal space was sampled by a single Γ point.

The MD simulation was conducted in a NVT ensemble with a time step of 1 fs. The total time of MD simulation reaches up to 33 ps, when the energy release becomes relatively stable (Figure 4). Initially, eight RDX molecules (totally 168 atoms) were placed in an orthorhombic supercell of $a = 13.182 \text{ \AA}$, $b = 11.574 \text{ \AA}$ and $c = 10.709 \text{ \AA}$ (which corresponds to a mass density of 1.81 g/cm^3), with its crystalline configuration [29]. During the MD simulation, there is neither symmetry constraint nor rigid molecule approximation. In other words, all degree of freedoms are allowed to relax within the given simulation supercell.

3. Results and discussion

The validity of the present computational scheme was confirmed via calculations on the gas phase molecule and crystalline solid of RDX. The theoretical bond lengths calculated for the RDX molecule were roughly in accord with experimental values [17,29], with about 2.8% deviation in average. For example, the computed length of C–N bond is 1.436 \AA , compared to 1.443 \AA by experiment; N–N bond length is 1.326 \AA from our calculations and 1.351 \AA from experiment, respectively. The lattice energy of RDX molecular crystal [29], defined as energy difference between gas phase and condensed phase, was 1.05 eV per molecule from our calculation, reasonably close to the experimental data of about 1.35 eV [31].

Figure 1 presents snapshots at different simulation time (0, 1, 5, 10, 20 and 30 ps). A quick look of these snapshots shows that the RDX molecules first dissociate into some fragments with a variety of chemical formula.

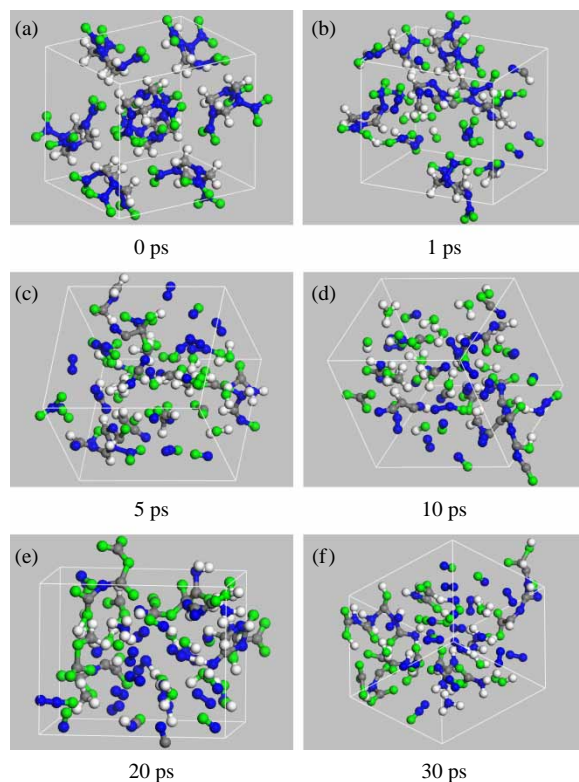


Figure 1. (Colour online) Snapshots with different simulation times. In these snapshots, white balls stand for hydrogen atoms, and gray ones are carbon, blue ones are nitrogen, green ones are oxygen.

In the subsequent reactions, these intermediate fragments further decompose into small molecules (such as N_2 and H_2O), groups (like NO_2) or molecular fragments. Afterwards, some long-chain molecular fragments (such as $\text{C}_5\text{H}_4\text{N}_5\text{O}_3$ at 5 ps and $\text{C}_3\text{H}_3\text{N}_2\text{O}_2$ at 10 ps) emerge and their chemical composition varies with simulation time via constantly losing/capturing other atoms/groups. Within the entire simulation time of 33 ps, we have not observed complete decomposition of these long-chain compounds, which might be the embryo of the carbon clusters as the long-term products of condensed phase. In addition to those main products (N_2 , H_2O , CO_2 , etc.), other minor groups like H, CH_3OH , H_2CO_3 , HCO_3 , NHCO , etc. were found with less population.

Figure 2 shows time-evolution of the populations for those key products up to 33 ps; Figure 3 summarizes the average populations of the key products within our simulation supercell during different time intervals. One can find that N_2 is the most abundant product and NO, H_2O are also the main products with a little less yields within the entire simulation time (33 ps). The number of N_2 molecules first increases rapidly with time then it becomes rather stable. During our simulation, the mean population of NO is rather stable and it slightly reduces with time.

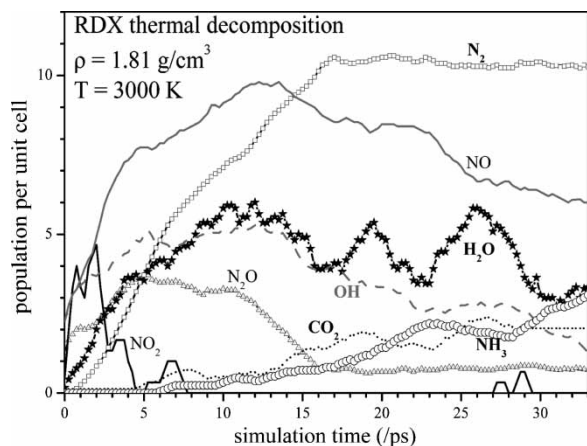


Figure 2. Time evolutions of the populations of key products at temperature = 3000 K at the density = 1.81 g/cm^3 .

With increasing time, populations of CO_2 , H_2O and NH_3 slowly increase, while those of OH and N_2O slowly decrease.

NO_2 groups emerge at the early stage of decomposition but they disappear rapidly when the reaction further proceeds. In other words, NO_2 is identified as one of the key intermediates from the present simulation, in agreement with previous guesses for the dissociation of the $\text{N}-\text{NO}_2$ bond [7,11,13,20,21]. For instance, using the first-principles gradient-corrected DFT and a simple transition state theory analysis, Wu and Fried [13] reported

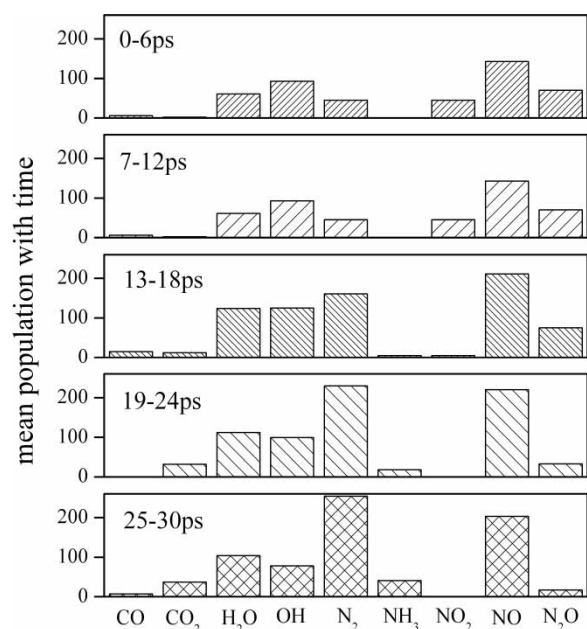


Figure 3. Mean populations of products with time from 0 to 30 ps at different time intervals.

the path of $\text{N}-\text{NO}_2$ bond rupture, that is, the NO_2 groups' formation is the dominant channel in gas phase thermal RDX decomposition. Similar behaviour was found for N_2O , with abundance higher than that of NO_2 . It might come from reactions involved NO_2 and also plays a role as an intermediate product. In previous studies of the decomposition mechanism of α -HMX [24,30], NO_2 was found to be the most important intermediate product during reaction. At the early stage, the $\text{N}-\text{NO}_2$ bonds break first and then the dissociated NO_2 groups further initiate chemical reactions. It is noteworthy that the $\text{N}-\text{NO}_2$ bond was found to be the most sensitive bond in the RDX crystal under hydrostatic compression from a recent DFT calculation [17].

In a previous ReaxFF-MD study by Strachan et al. [14], thermal decomposition of RDX was simulated within different conditions: one of these conditions is similar to the present one. Similar to our results, they observed key products of N_2 , H_2O , CO_2 and CO , as well as intermediate product of NO_2 . However, the NO groups were not mentioned in their paper. In another ReaxFF-MD simulation of shock-induced chemistry of RDX [26], NO groups appeared as one of the final products and their population depends on impact velocities.

Mulliken population analysis was also performed to examine the charge status of the chemical groups found in the simulation. We found that each NO group carries about one positive charge (0.937 electron charge at 3 ps), each NO_2 groups has about one positive charge (0.927 electron charge at 3 ps), OH group one negative charge (-0.906 electron charge at 3 ps). Since accumulative positive/negative charge usually serves as the centre of chemical reactions, we suggest that those charged groups might promote the chemical reaction for further decomposition.

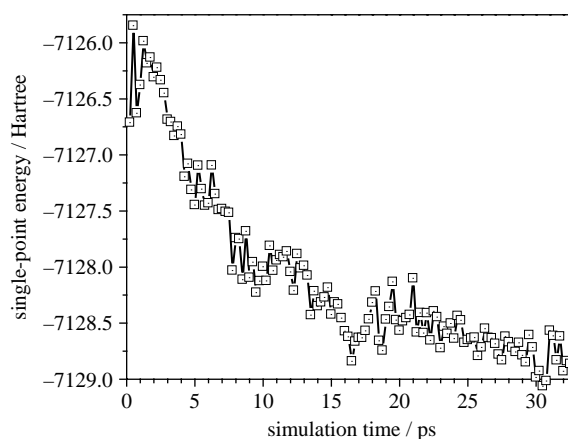


Figure 4. Evolution of single-point energy of simulation supercell with time.

We further examined the energy transformation mechanism during thermal decomposition. Figure 4 shows the evolution of single-point energy computed for the simulation supercell during the entire simulation time of 33 ps. It is found that the initial decomposition result in a sharp rise of system energy, then those intermediate products trigger further reactions between the fragments and RDX molecules. Consequently, RDX molecules further decompose into smaller molecules, groups and molecular fragments, releasing large amount of reaction heat. At the very early stage of decomposition, the system releases enormous energy (about 2.5 hartree within the simulation supercell, equivalent to 0.4 eV per atom). About 90% of reaction heat was released in the first 15 ps of the simulation time. Afterwards, the total energy of system becomes rather stable only with small-amplitude oscillations.

4. Conclusion

In summary, we simulated the thermal decomposition of RDX of 1.81 g/cm^3 at 3000 K via DFT MDs. We found that H_2O , OH, N_2 and NO_2 are the dominant products of thermal decomposition, and CO, CO_2 , CNO and N_2O emerge as minor products. The amounts of major products, i.e. H_2O , CO_2 and N_2 , generally increase with time. Carbon-based long chain molecular fragments are observed, whose chemical compositions vary with time. Charged NO_2 and N_2O groups are found as the intermediate product, which are formed in the initial stage and disappear in further reaction. We suggest that those charged groups may promote the chemical reaction for further decomposition. DFT–MD simulations with longer timer scale and higher theoretical level are still underway to further understand the decompositions of RDX and other energetic materials.

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