Decomposition Mechanisms of α-RDX Crystal Under High Temperature Coupled with Detonation Pressure by Ab Initio Molecular Dynamics Simulations

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Abstract: The initiation and subsequent decomposition mechanisms of α-RDX crystal under high temperature (3000 K) coupled with detonation pressure (34.5 GPa) were studied by ab initio molecular dynamics simulations. The crystal structure of RDX was relaxed using two types of van der Waals corrections such as PBE-G06 and PBE-TS functional at ambient conditions. The results indicate that the PBE-G06 functional is much suitable for studying α-RDX. Results show that the decomposition of α-RDX is triggered by the homolysis of the C—H bond. The DOS clearly validates that the C—H bond is broken. The elimination reaction of HONO during the decomposition is observed. The primary reactions for producing NO2, NO, N2O, N2, HONO, N2O3, H, O—H, H2O, and CO2 occur at very early stages. After the initiation of RDX, there are three different subsequent decomposition pathways. There are three main interesting subsequent decomposition paths include: (1) the C—N bond homolysis triggers the other C—N bonds of this ring to break; (2) the dissociation of N—NO2 bond releases NO2 gas; (3) the H radical attacks the O atom to release O—H radical by forming O—H bond.

Key words: Ab initio molecular dynamics; α-RDX; initiation reaction; decomposition

1 Introduction

It is particularly a challenge to obtain a clear picture on the decomposition mechanisms of condensed phase explosives under extreme conditions due to their complex behaviors and danger in experimental measurements. The atomistic simulation is an effective way to model the physical and chemical properties of complex solids under extreme conditions at the atomic level as a complement to experimental work. Recently, the application of ab initio molecular dynamics (AIMD) method in studying the decomposition mechanisms and sequences of the explosives at realistic reaction temperatures and pressures has seen tremendous progress.

1,3,5-Trinitro-1,3,5-triazocyclohexane (RDX) is one of the most important nitramine explosives widely used for both civilian and military applications. The decomposition of RDX has been investigated by a number of groups using both experimental and theoretical methods. These studies, which were conducted under a variety of ambient- and high pressure environments, discuss a number of decomposition mechanisms that RDX may undergo; these include the loss of NO2 groups, the cleavage of the C—N bond to create CH3—N2—O2 species, as well as whether the decomposition is a unimolecular or bimolecular process. There is an obvious difference between the two researches, so it is necessary to study the initial and subsequent decomposition mechanisms of RDX under extreme conditions further. In this work, AIMD was used to systematically study the reactive events of the initial decomposition and following reactions of crystalline α-RDX under high temperature (3000 K, which is the flame temperature of α-RDX) coupled with high pressure (34.5 GPa, which is the detonation pressure of α-RDX).

2 Simulations and Computational Method

All calculations were performed in the framework of DFT using norm-conserving pseudopotentials and a plane-wave expansion of the wave functions based on the CASTEP code. The exchange and correlation were treated with the generalized gradient approximation (GGA), using the functional form of Perdew-Burke-Ernzerhof (PBE) method. To correct DFT for neglecting van der Waals (vdW) interaction, Grimme (G06) and Tkatchenko and Scheffler (TS) correction to the PBE functionals (labeled as PBE-G06 and PBE-TS) were used. RDX belongs to the orthorhom-
bic space group $P2_1/n$ with experimental lattice constants ($a = 13.18 \text{ Å}, b = 11.57 \text{ Å}, c = 10.71 \text{ Å}$). One unit cell consists of four molecules (168 atoms). Both geometry and cell volume were optimized using periodic DFT with vdW corrections (DFT-D). A plane wave cutoff of 500 eV for molecular dynamics and 750 eV for geometry and cell optimizations was utilized. Constant temperature AIMD simulations were performed using the Car-Parrinello scheme\textsuperscript{21} with Nosé-Hoover thermostats\textsuperscript{22} for nuclei. Time steps 1 fs and 2 fs were used for the integration of the equations of motion during production and equilibration runs, respectively. The results indicate that 1 fs is much more suitable. The time step of 1 fs is chosen to longer time simulation of 20 ps. The convergence criteria were set to a $1 \times 10^{-5}$ eV energy difference for geometry optimization and a $1 \times 10^{-3}$ eV energy difference for DFT-MD simulation. Structures for the $\alpha$-RDX were optimized individually before AIMD simulations. The procedure for the DFT-MD simulations was as follows; First, the system was equilibrated at 298. 15 K for 10 ps using NVT. Then, AIMD simulations were carried out using NPT at 3000 K coupled with 34.5 GPa based on this equilibrated system. The simulation time was 20 ps for the AIMD simulations.

3 Results and Discussion

Here, the PBE-G06 and PBE-TS functionals to fully relax $\alpha$-RDX crystals at ambient pressure without any constraint were applied, respectively. Table 1 lists the experimental and relaxed cell parameters of $\alpha$-RDX crystal. It is found that calculated lattice parameters by the PBE-TS functional are 2.35%, 0.86%, 1.68% and 4.93% over the experimental parameters. The PBE-G06 calculation errors are 0.99%, 0.26%, 0.56%, and 1.72% for lattice constants $a$, $b$, and $c$, respectively. This indicates that the lattice parameters estimated by the PBE-G06 here are much closer to the experimental value than those by the PBE-TS. Therefore, the PBE-G06 functional is much suitable for studying $\alpha$-RDX.

Table 1 \ Comparison of relaxed lattice parameters of $\alpha$-RDX with experimental data under ambient pressure conditions

<table>
<thead>
<tr>
<th>method</th>
<th>$a \text{ /Å}$</th>
<th>$b \text{ /Å}$</th>
<th>$c \text{ /Å}$</th>
<th>cell volume/Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp.\textsuperscript{14}</td>
<td>13.18</td>
<td>11.57</td>
<td>10.71</td>
<td>1613.90</td>
</tr>
<tr>
<td>PBE-TS</td>
<td>13.49</td>
<td>11.67</td>
<td>10.89</td>
<td>1714.39</td>
</tr>
<tr>
<td>PBE-G06</td>
<td>13.31</td>
<td>11.60</td>
<td>10.77</td>
<td>1662.06</td>
</tr>
</tbody>
</table>

Note: Values in parentheses correspond to the percentage differences relative to the experimental data.

3.1 Initial Decomposition Mechanism

At 3000 K coupled with 34.5 GPa, the initial decomposition step of $\alpha$-RDX is the unimolecular C–H bond breaking to form hydrogen radical (Fig. 1). The H radicals then induced the cleavage of two C–N bonds in other $\alpha$-RDX molecule. The bond lengths of the two C–N bonds increase to 1.857 Å and 1.762 Å at first 3 fs, respectively. This suggests that the H radicals play a catalytic role in promoting subsequent decompositions.

![Fig. 1 Initial decomposition mechanisms of $\alpha$-RDX crystal at high temperature 3000 K coupled with detonation pressure 34.2 GPa](image)

To identify the breaking of intermolecular C–H bond, the density of states (DOS) of C and H atoms in RDX was investigated. Fig. 2 displays the DOS of the C and H states before and after the decomposition of $\alpha$-RDX. It is found that the variation trends for the DOS curves of the C and H states before the decomposition of $\alpha$-RDX are similar. But they have a few changes after decomposition. Three main strong peaks occur almost at the same energy in the DOS of the C and H states before and after decomposition of $\alpha$-RDX. Although their DOS peak height is almost the same before its decomposition, their peaks obviously reduce after its decomposition.

This may be due to the C–H bond cleavage in the decomposition process. Fig. 3 displays the DOS of the C and N states before and after the decomposition of $\alpha$-RDX. It is seen that the variation tendency for the DOS of the C and N states before the decomposition of $\alpha$-RDX is similar. All of the peaks occur at the same energy in the DOS of the C and N atoms states before its decomposition. This indicates that the two atoms are strongly bonded. However, after the decomposition of $\alpha$-RDX, some main peaks do not occur at the same energy. This clearly validates that the C–N bond is broken.

3.2 Subsequent Decomposition Process

After the initial decomposition, three subsequent decomposition processes take place, as displayed in Fig. 4. Three main interesting decomposition paths include: (1) the C–N
Fig. 2  DOS curves of the C and H states in the C—H bond before and after the initial decomposition of α-RDX

Fig. 3  DOS curves of the C and N states in the C—N bond before and after the initial decomposition of α-RDX

Fig. 4  Three subsequent decomposition paths after the initiation of α-RDX crystal
bond hemolysis triggers the other C—N bonds of this ring to
break; (2) the dissociation of N—NO₂ bond releases NO₂
gas; (3) the H radical attacks the O atom to release O—H
radical by forming O—H bond. However, the decomposition
processes are different from reported four different primary
decomposition pathways \(^{23-24}\). Although our primary
decomposition pathways do not include successive HONO elimina-
tion \(^{25}\), there exist the HONO fragments in decomposition
products of α-RDX. In our simulation, it is not observed that
an oxygen migrates from NO₂ to its neighboring C tom, which
was reported by Botcher et al. \(^{24}\). There are a large number of
subsequent generated intermediates in the unimolecular de-
composition of α-RDX. Among them, Int 1, Int 2, and Int 3
are main intermediates. Compared with Int 2 and Int 3, the
incidences of Int 1 are very low. This indicates that the N—NO₂
fragments are very active. There are several different heterocy-
amic compounds observed in the decomposition. These hetero-
cyclic products can transform to form chain fragments. The
heterocyclic C₃N₃ is most likely to occur. This demonstrates
that the heterocyclic C₃N₃ is much more stable than the
N—NO₂ fragments.

3.3 Decomposition Products

Fig. 5 shows the time evolution of the population of key
decomposition products during the cleavage of α-RDX. The
RDX molecules delayed quickly at the beginning of the decom-
position. All the nitro groups released fast at about 0.05 ps and
the number of the nitro groups reaches a maximum of 10. Then
the NO₂ radicals decayed quickly within about 0.1 ps. At the
same time, the number of HONO radicals increased to reach a
maximum of 5 at about 0.05 ps. As the HONO is a very active
intermediate, it decomposed rapidly to yield HO and NO frag-
ments. The concentration of HONO was consumed practically
during the time of about 0.1 ps. After the NO₂ and HONO
radicals disappeared, nitric oxide accumulated quickly to reach
a maximum concentration of 5 molecules within about 0.1 ps.
 Afterwards they slowly reacted to form N₂, N₂O, and NOH.
Fig. 5 provides a proof for the NO₂ and HONO intermediates
decomposing to release NO. NO₂ can react with H to form
NO. At the decomposition end of the NO₂ radicals, the con-
centration of N₂O₄ reaches the maximum. But they strongly
fluuctuated due to high oxidation activity. N₂O₄, a prototypi-
-cal species of weakly bonded systems, has been the subject of
intense theoretical interest \(^{26-28}\). NO₂ radical is known to exist
in the crystal as a dimer N₂O₄ and forms via addition of two
NO₂ radicals \(^{29}\).

At about 2 ps, the concentration of nitrous oxide reaches the
maximum, but they strongly fluctuates due to high oxidiza-
tion activity. The main intermediates during the decomposi-
tion of RDX contributed to the production of nitrogen gas. The
concentration of nitrogen gas gradually increases, reaching 15
molecules at 14 ps after the initiation of RDX, then decreases
12 molecules during the whole simulation time. Among the
five products, N₂O is the most unstable one and its mean life-
time survived in the system is about 11.8 ps. N₂O is induced by
the hydrogen radical to form N₂. The first CO₂ was released at
about 1.9 ps. The variation tendency for the concentration
of CO₂ is stable at the whole decomposition stage. CO₂ is
found to be in significantly smaller amounts than other species
described above. Although many C—O bonds are formed, no
more CO₂ is generated in the subsequent simulations. At the
beginning of the simulation, the O—H fragment is formed.
Then the concentration of O—H increases to 17 molecules.
O—H is induced by the hydrogen radical to form H₂O. The
concentration of H increases at the maximum of 4 molecules.
H₂O forms fast at the beginning and the number of H₂O rea-
ches the maximum of 10 molecules at 6 ps. Then the concen-
tration H₂O quickly decreases and reaches stable after 12 ps.

4 Conclusions

(1) The decomposition of α-RDX at 3000 K coupled with
34.5 GPa is triggered by the homolysis of the C—H bond.
(2) The HONO elimination reaction during the decomposi-
tion is observed.
(3) The primary reactions of producing NO₂, NO, N₂O,
N₂, HONO, N₂O₄, H, O—H, H₂O, and CO₂ occur at very
early stages
(4) After the initiation of RDX, there are three different
decomposition pathways, their decomposition processes can
be described by Fig. 4 shown in the text.

References:

Decomposition Mechanisms of α-RDX Crystal Under High Temperature Coupled with Detonation Pressure by Ab Initio Molecular Dynamics Simulations


运用从头算分子动力学模拟高温耦合爆轰压力条件下α-RDX的分解机理

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摘 要：运用从头算分子动力学模拟了α-黑索今(RDX)晶体在高温(3000 K)耦合爆轰压力(34.5 GPa)下的初始和随后的分解机理。采用两种范德瓦耳斯的修正方法(PBE06和PBE-TS)环境条件下对RDX的晶体结构进行了优化。结果表明, PBE-TS非常合适优化RDX。RDX分解中,C—H 键均裂引发α-RDX分解。过程的结果也证明了C—H 键的键合现象。分解过程中发生了HONO 的消去反应。产生NO₂, NO, N₂O, N₂, HONO, N₂O₄, H₂O, H₂O₂和CO₂为主要反应,发生在早期阶段。同时, RDX分解后的三种不同的分解途径分别为(1) C—N 键断裂引发环中其它C—N 键断裂; (2) N—NO₂键断裂并且释放NO₂气体; (3) H 自由基和氧原子碰撞形成O—H 键后释放O—H 自由基。

关键词：从头算分子动力学; α-黑索今(RDX); 初始反应; 分解

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