Analysis of Chemical Reaction Process after Pentaerythritol Tetranitrate Hot Spot Ignition

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ABSTRACT: In this paper, ReaxFF force field combined with molecular dynamics method was used to study the ignition, deflagration, and detonation of pentaerythritol tetranitrate (PETN) induced by hot spots. The hot spot is 5.6% of the total volume. When the hot spot temperature is 1000 K, the deflagration and detonation of PETN cannot be observed in the simulation time of 200 ps. When the hot spot temperature is 2000 K, it corresponds to the heating time of 20 to 50 ps, deflation and detonation were observed. During hot spot ignition, the products of decomposition of the condensed phase PETN are dominated by NO2 and HONO. The energy required for the C−C bond and C−ONO2 bond cleavage in PETN is high, resulting in only a small amount of CH2O and NO3 during the reaction. Small nitrogen-containing molecules (such as NO2, NO3, HONO, HNO3, etc.) mainly exist during thermal equilibrium, while the number of N2 increases sharply during the thermal runaway stage, and a small amount of NH3 and NH2 are also produced. H2O molecules are formed before CO2 and N2 are produced, and the number always dominates. During the thermal runaway, the entire system can maintain a spontaneous reaction, resulting in a sharp rise in temperature of about 2500 K in 20 ps. During this phase, the catalytic effect of H2O accelerates the formation of CO2 and N2 due to the near Chapman–Jouguet point in the crystal. PETN is a weak oxygen balance explosive that results in a small amount of CO and H2 production during the thermal instability phase. When the reaction is balanced, the relative molecular mass is close to or exceeds that of PETN. The product is only less than 1% of the total mass fraction, while the small molecule product is as high as 78%, and some relative molecular masses are [75,225]. The intermediates account for about 21%. Rapid and complex reaction events make it difficult to accurately predict the structure of these intermediates by existing experiments and calculations, which will be the focus of future research.

1. INTRODUCTION

Ignition of energetic materials can be achieved through different starting conditions, such as heat,1 impact,2,3 laser,4,5 and so on. Under ignition conditions mentioned above, the region being high temperature inside the solid is called “hot spot” and is used to describe the prerequisite for ignition. The collapse6 and misalignment of the cavity in the condensed energetic materials, causing heating7 due to viscosity, shear band,8 and particle friction,9 etc. can produce hot spot. When the “hot spot” region is large enough and the temperature in the “hot spot” is high enough, it is possible to trigger spontaneous ignition of energetic materials. It is generally believed that the self-sustaining ignition process triggered by hot spots is accompanied by complex chemical reactions. If the energy released during the chemical reaction is higher than the energy consumed by heat loss, the ignition process will grow to form a deflagration, detonation, burst, and other phenomena. The critical hot spot temperature and the hot spot size required for ignition of the energetic materials in the condensed phase cannot be directly measured experimentally, while molecular dynamics (MD) simulation method can be able to reveal the complex chemical reaction process induced by ignition on the microscale, providing a new approach to analyze the physical chemical process due to hot spots of energetic materials.

Pentaerythritol tetranitrate (PETN) is an organic nitrate commonly used as a kind of a high-explosive reagent in detonators, an ingredient in a high-energy mixture,10 and drugs11,12 for heart disease. PETN has only one crystal form, namely PETN−I,13 at room temperature and normal pressure, while PETN−II,14 also exists at high temperature and PETN−III,15 exists under the high pressure of 6 GPa. Under the action of external stimuli (heat, impact, laser, and so on.), the atomic mechanism and dynamic response of most energetic materials are incomplete, possibly with several coexisting reaction pathways throughout the decomposing process. The bond

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fracture of O−NO₂ in PETN, which acts as the initial reaction mechanism of PETN decomposition, has been verified in the decomposition process of gas-phase and condense-phase PETN.16 Zybina et al.17 explained that the initial decomposition path of PETN is the O−NO₂ bond fracture from the perspective of steric hindrance. Wu et al.18 explained from the perspective of molecular collision: during the collision, the initial decomposition path of PETN is the break of the O−NO₂ bond. By studying the thermal decomposition of PETN, Ng et al.19,20 found that the thermal decomposition and sublimation of solid PETN competitively proceed. They also pointed out that the main starting path of PETN decomposition depends on the triggering methods, as follows: stimulation by slow heat or low energy will produce a large number of NO₂, the number of NO₂ caused by strong impact is considerably larger than that of NO₂ while there is no much different of production of NO₂ and NO₂ when faced with weak impact, and high-energy lasers can cause ONO₂. Previous studies have shown that the starting of the impact of PETN strongly depends on the orientation of the crystal axis relative to the direction of impact.21 When PETN crystals are affected in the directions of (110) and (001), strong light emission is observed, which is identified as the chemiluminescence of NO₂ ions.22,23 The difference is that NO₂ and NO₂ formation are observed by impact in the direction of (110), while NO₂ forms dominantly by impact in the direction of (001).24 This is because the C−ONO₂ bond is parallel to the impact orientation arrangement with starting impact along the direction of (110), more kinetic energy can be acquired than that from the CO−NO₂ bonds, resulting in a lot of NO₂ formation; on the contrary, in terms of the impact in the direction of (001), the CO−NO₂ bond is parallel to the impact orientation arrangement, thus NO₂ is the main initial products of decomposition.

Landerville et al.25 simulated the super-high-speed collision of dual-molecule PETN and pointed out that in high-speed collisions, chemical reactions are driven by dynamics (including mechanical deformation, thermal vibration, local excitation, etc.) rather than temperature; Budzien et al.26 conducted the dynamics simulation of the impact of PETN, NO₂, CH₂O, and CH₂NO₂ were also observed after the generation of NO₂. Recently, a series of experiments and computational simulations of a series of laser-illuminated PETN samples in gas phase27 mixed with photosensitive additives and condensed phase2,28 have proposed a new approach to decomposition induced by resonant light and new questions about the initial chemical reactions. Yu et al.27 pointed out that the production of NO₂ in the PETN in the excited electronic state happened after the NO₂ on the contrary, if the PETN molecule is only thermal disassociated on the surface of the ground state, the main decomposition channel should be the dissociation of O−NO₂ bond, resulting in NO₂. Kulka et al.29,30 studied the selective light excitation of the laser-induced PETN molecule, which is a two-stage decomposition process, including the light excitation of the PETN molecule (which may be deformed by the out-of-plane bending of the NO₂ group) and subsequent thermal stimulation, the separation of the molecule from and its excitation state as well as the formation of triple states and active particles (most likely the NO₂ free radicals).

However, previous studies have not provided details of the chemical reactions of decomposition after the ignition of the condensed phase PETN, and this paper will carefully analyze the chemical reactions after PETN ignition to provide valuable information for the ignition of the energetic materials. Considered are the three steps in the ignition experiment of energetic materials, as follows: (1) external stimuli (heat, impact, laser, etc.) provide heat for some solid materials to form hot spots; (2) when the external stimuli are removed, points or delay are observed until the reactive chemicals reach the critical point; and (3) after reaching the critical point, spontaneous ignition and possible deflagration can be achieved. By using the combination of molecular dynamics with the ReaxFF/lg force field and through providing continuous heat to a small part of the PETN monocrystal to obtain the hot ignition of different time durations, this paper stimulated chemical reaction process after PETN ignition under different thermal pulse conditions, hoping to explain the detonating and explosion mechanism of energetic materials at the atomic level and to provide insight for the ignition of hot spots and ignition-induced deflagration and detonation of energetic materials.

2. SIMULATION DETAILS

Based on the principle of the first principle, ReaxFF reaction force field can describe the formation and fracture of intermolecular bonds of energetic materials under extreme conditions through the relationship between bond length, bond level, and bond energy, as well as the dynamic transfer of charge between atoms.29 ReaxFF/lg30 adds a description of the London dispersion force under the foundation of ReaxFF, i.e., having revised the long-range interaction force between molecules, thus it describes the structure and density of molecular crystals more accurately, and the calculated crystal structure and state equation show good consistency with the experimental results. ReaxFF/lg has been used to study various physical and chemical properties of energetic materials31−33 and has achieved the expected results.

In this paper, crystal PETN−I under room temperature and normal pressure is used as the research object, the initially monocrystal structure of PETN is derived from the Crystal Database of Cambridge University (CCDC), which contains two molecules. To obtain a higher computational accuracy35 and to fully observe the chemical reaction process after the ignition of PETN hot spots, 6 × 6 × 6 supercells are constructed with an initial density of 1.827 g cm⁻³. Figure 1 shows the PETN supercell and monomolecular model. The supercells are structurally optimized by energy minimization, then the crystal is placed in the NVT ensemble (300 K) for 10

Figure 1. Structures of the PETN molecular and supercell. The ball and stick models represent the hot spot region. The C, H, O, and N are presented by grey, white, red, and blue balls, respectively.
ps, and later in the NPT (300 K, 0 GPa) for 30 ps to optimize atomic coordinates. After optimization, the density of the PETN supercell is 1.789 g·cm\(^{-3}\), which is close to the experimentally measured density\(^{36}\) of 1.773 g·cm\(^{-3}\). PETN supercells (2 \(\times\) 2 \(\times\) 3) are selected as the hot spot part (the ball and stick model shown in Figure 1), giving the hot spot part different heat durations, using NVT ensemble to maintain the temperature of the hot spot part at 1000 and 2000 K, NVE ensemble is used in the other parts. In this article, the duration of the thermal pulse varies between 20 and 50 ps. Once it reaches the thermal duration, the entire system is placed under the NVE ensemble to simulate the chemical reaction process after PETN ignition. The simulation process uses conditions of periodic boundary with a time step of 0.025 fs. These procedures mentioned above are simulated using LAMMPS (large-scale atomic/molecular massively parallel simulator)\(^{37,38}\) with the ReaxFF/\(\lg\) potential.

3. RESULTS AND DISCUSSION

3.1. Effect of Thermal Duration on Ignition of the PETN Crystal. Figure 2 shows the relationship between the thermal duration (\(t_{\text{heat}}\)) and the temperature of ignition of hot spot. When the temperature of ignition of hot spot is 1000 K, only a small amount of chemical reaction occurs within 200 ps after ignition (more details are shown in the Supporting Information S1), hence only the temperature of ignition of hot spot of 2000 K is listed in Figure 2. Because energy is transferred from hot spot to non-ignited regions, the temperature of non-ignited regions increases until the whole system is balanced. In all simulated cases, the temperature of the PETN crystal gradually increases, even above the temperature of Chapman–Jouguet (CJ) point of the PETN\(^{39,40}\) (\(T = 4200\) K). According to the hot spot ignition theory\(^{41}\) for the PETN crystal with a hot spot size of less than 0.1 \(\mu\)m, the corresponding temperature should not be less than 850 K, and the thermal equilibrium temperature shown in Figure 2 is obviously higher than 850 K, therefore, phenomena of PETN deflagration and even detonation can be observed. When \(t_{\text{heat}}\) is higher than 40 ps, the ignition delay observed is short; the PETN crystal jumps directly to the thermal instability state after short-lived thermal balance and when \(t_{\text{heat}}\) is equal to 20 ps, the ignition delay is longer, while at 170 ps, the temperature of the PETN crystal exceeds 2000 K. So, this paper focuses mainly on the case where \(t_{\text{heat}}\) equals 30 ps. When \(t_{\text{heat}}\) is equal to 30 ps, the entire crystal is first balanced to 1350 K (60 ps) at the end of the thermal duration and then it slowly increases to 1850 K (110 ps), this is due to the comprehensive influence of the initial energy transfer and heat-releasing reactions in the ignition region. After 130 ps, the whole crystal can react spontaneously, resulting in a sharp increase in temperature to about 2500 K within 20 ps, and a sudden change in the temperature curve indicates that the net heat-releasing reaction exceeds the heat-absorbing reaction in the reaction region, which can maintain the front of the spontaneous reaction.

Figure 3 shows the temperature and pressure of the system’s thermodynamic variables over time. In statistical mechanics, temperature is related to the kinetic energy of the system, and pressure is related to temperature. The temperature rise is
accompanied by the pressure rise, and the reaction is complete at about 12 GPa.

Figure 4 shows the evolution curve of system potential energy (PE) and kinetic energy (KE) with time. It can be seen that the heat pulse ignites the system to a very high energy state to promote the hot spot ignition. In the initial stage, due to the presence of external heat sources, both potential and kinetic energy slowly increase. In the thermal equilibrium phase (between the dotted lines A and B), the potential energy is slowly transferred to the kinetic energy, indicating that the total energy of the system is conserved. In the thermal instability state, the kinetic energy increases rapidly with the decrease of potential energy. At 155 ps, the potential energy of the system rises slightly, which may be affected by the periodic boundary conditions, but the chemical reaction has been completed at this time, and the increase in potential energy does not affect the analysis results.

3.2. The Oxynitride Product. During the time when gas-phase PETN decomposes, the activation energy of O−NO₂ bond is low (35 kcal·mol⁻¹ to 37 kcal·mol⁻¹) while the pre-exponential factor is higher (lgA = 10¹⁷ to 10¹⁸ s⁻¹),²⁶ so O−NO₂ bond fracture is the most advantageous decomposition path for PETN, while the decomposition of condensed-phase PETN is more complex. Table 1 shows that in this process, various compounds are produced. Table 2 shows the bond

Table 1. Chemical Reactions and Intermediates

| number | reaction | molecular |
|--------|----------|-----------|
| 1      | C(CHONO₂)₄ → C(CHONO₂)₃CH₂O + NO₂ | C₅H₈O₁₀N₃ |
| 2      | C(CHONO₂)₄ → C(CHONO₂)₂(CH₂O)₂ + 2NO₂ | C₅H₈O₁₀N₃ |
| 3      | C(CHONO₂)₄ → C(CHONO₂)₂ + NO₂ + CH₃O | C₅H₇O₁₀N₃ |
| 4      | C(CHONO₂)₄ → C(CHONO₂) (CH₂O)₃ + 3NO₂ | C₅H₈O₉N₂ |
| 5      | C(CHONO₂)₄ → C(CHONO₂)₂CH₂ + NO | C₅H₇O₁₀N₃ |
| 6      | C(CHONO₂)₄ → C(CH)(CHONO₂)₂ + HONO | C₅H₇O₉N₃ |
| 7      | C(CHONO₂)₄ → C(CH)(CHONO₂)₂ + NO₂ + OH | C₅H₇O₁₀N₃ |
| 8      | C(CHONO₂)₄ → C(CH)(CHONO₂)₂ + 2HONO | C₅H₇O₁₀N₃ |

Table 2. Bond Order Cut-off Values for Various Atom Pairs

| atom | C | H | O | N |
|------|---|---|---|---|
| C    | 0.55 | 0.40 | 0.65 | 0.30 |
| H    | 0.55 | 0.40 | 0.65 | 0.30 |
| O    | 0.65 | 0.55 | 0.45 |   |
| N    | 0.45 | 0.55 | 0.45 |   |

Figure 5 describes the time evolution curve of the product after the loss of small molecular nitrogen compounds.
molecular nitrogen-containing compounds during PETN decomposition. Within 30 ps (left side of the dividing line A in Figure 5), there are numerous C₆H₈O₁₀N₃ and C₆H₇O₉N₃, indicating that during the thermal pulse, the decomposition of the condensed-phase PETN is dominated by the generation of NO₂ and HONO. After removing the thermal pulse, the reaction of the HONO is an exothermic reaction since the total energy in the system remains unchanged, i.e., further promoting the occurrence of the chemical reactions. During the thermal equilibrium (between dividing lines A and B), the items shown in Figure 5 reach a peak and then gradually decreases, C₆H₈O₁₀N₃ peaked first, and C₆H₇O₉N₃ peaks at the highest. The number of C₅H₈O₉N₃, C₅H₇O₉N₃, and C₆H₈O₁₀N₃ is always very small, indicating that the reaction with C–C bond breaking, loss of three NO₂, and the generation of NO₃ is difficult to occur. This is due to the following: (1) Although the C–C bond of PETN is a single bond, but the bond length is only 0.91 smaller than 1.16 of O–NO₂, so the energy need for C–C breaking is higher because the C–C bond is not easy to break. (2) Three NO₂ lose at the same time, meaning that more energy is needed. However, this study researches on the ignition of hot spot in which instantaneous energy threshold is too low to support the reaction, where PETN decomposition induced by laser-induced resonant light²⁸ may exist. (3) The energy required for C–ONO₂ bond fracture to generate NO₃ is 67 kcal·mol⁻¹ to 77 kcal·mol⁻¹, which is nearly twice as much as the energy required for O–NO₂ bond fracture,¹⁶,²⁵ so the number of C₆H₈O₁₀N₃ is relatively small. The number of the other three products (C₆H₇O₉N₃, C₅H₈O₉N₃, and C₆H₈O₁₀N₃) is medium, which is reasonable because they all undergo a secondary reaction and belong to the reaction intermediate. These reaction products are all decomposed into stable small molecular products during the thermal instability phase.

Figure 6 demonstrates the time evolution curve of small nitrogen-containing molecular products over time during the simulation process (excluding N₂, which will be discussed as a stable end product in the next section). Within 30 ps, nitrogen-containing small molecular products in the system are mainly NO₂ and HONO, the number of NO₂ is always higher than the number of HONO but with no obvious advantage. This is due to the generation of NO₂ during heat ignition by the reaction 1 and 2 shown in Table 1, that is, a part of PETN breaks one O–NO₂ bond, another part breaks two O–NO₂ bonds, while the number of HONO is mainly determined by the reaction 6. During the thermal balance (between the dashed lines A and the dashed lines B in the figure), the number of nitrogen-containing products increases with no NH₃ and NH₂ observed at this stage, and the number of NO₂, HNO₃, HONO, and NO₃ peaks at the end of the thermal balance. What worth noting is that NO₃ appears late and it remains at a low level, which confirms the fact that the reaction 5 is difficult to occur, as shown in Table 1. During the thermal instability state, NH₃ and NH₂ begin to appear but in a small quantity, other nitrogen-containing products are gradually decomposed and are converted into other stable gaseous products like N₂.

3.3. Steady Gaseous Product. In PETN molecules, O is mainly stored in the NO₂ and NO group, the formation of stable gaseous products can be seen as the process of O transfer from NO₂ and NO to C and H. Figure 7 shows the time evolution curve of stable gaseous products from ignition to thermal runaway. The H₂O molecule is formed before producing CO₂ and N₂, and the quantity always occupies an absolute advantage, and this chronological order can be explained by the relative distance between atoms, the closer the reactants are, the shorter the time required to form the products. During thermal ignition, NO₂ and H₂ are generated, and the close proximity of these two creates the conditions for the production of H₂O. That is, it is easy to get the following reactions: 2H + NO₂ → HONO + H → H₂O + NO. The reduction of NO and NO₂ to N₂ is a much slower process because the distance of N atoms is relatively large in PETN, and N has much less fluidity. As it can be seen from Figure 7, N₂ appears at the moment about 100 ps.

During thermal equilibrium, there is only a small increase in other gaseous products except H₂O. Since PETN is a weak negative oxygen-balanced explosive (OB = −10%),⁴² there is a small amount of CO and H₂ formation during thermal instability. In contrast to Figure 6, oxynitride is the main small molecular products before thermal instability but no carbon oxides such as CO and CO₂, from which C is known to be generated primarily by capturing O from HO to form CO and CO₂ rather than directly capturing NO and NO₂. During
Within 100 ps, the PETN crystal is still in the thermal equilibrium stage, and the proportion of PETN molecule weight is relatively high. PETN decomposition releases products such as NO₂ and HONO, resulting in an increase in the proportion of the molecular weight of the product between 0 and 75, while the weight fraction of reaction intermediates that lose NO₂, NO, HONO, etc. also begins to increase, corresponding to the blue and green lines shown in Figure 8. In the thermal instability stage, there are fewer products with relative molecular weight close to or exceeding PETN only occupying less than 1% of the total weight fraction, while the proportion of small molecular products is as high as 78%, and some intermediates with relative molecular weight in [75,225] occupy about 21%. Existing experiments and computational methods are unable to accurately predict the specific chemical formula of these intermediates, because the explosion process of condensed energetic materials involves a variety of physical chemical reactions, and 200,000 reaction events are recorded during this simulation time (190 ps), which accentuates the complexity of the reaction. In the whole reaction process, no cluster structure similar to RDX, TATB, and so on is observed, and the formation of cluster structures will inevitably slow down the reaction process, which may be one of the reasons for the higher PETN sensitivity.

4. CONCLUSIONS

By combining with ReaxFF/fg force field with molecular dynamics, the processes of the ignition, deflagration, and detonation of PETN induced by hot spot are studied in this paper. For hot spot with a volume of 3.6% and a hot spot temperature of 1000 K, the deflagration and detonation of PETN are not observed. When the hot spot temperature is 2000 K, deflagration and detonation are both observed in the PETN crystal corresponding to the heating time of 20 to 50 ps. The whole crystal during the thermal instability stage can maintain the spontaneous reaction, resulting in a sharp rise in temperature to about 2500 K within 20 ps.

During the thermal pulse, the condensed-phase PETN is decomposed mainly into NO₂ and HONO, and no interaction of hydrogen bonds between molecules is observed. The energy required for the break of the C–C bond and C–O bond in PETN is higher, and only a small amount of CH₂O and NO₂ are produced during the reaction. Small nitrogen-containing molecules (e.g., NO₂, NO₃, HONO, HNO₃, etc.) mainly exist during thermal equilibrium, while the number of N₂ increases dramatically during the thermal instability stage, meanwhile there is a small amount of NH₃ and NH₂. H₂O molecules are formed before CO₂ and N₂ are produced, and the quantity always dominates due to NO₂ and H generated during thermal ignition, and their close proximity creates the conditions for producing H₂O. During the thermal instability stage, the catalytic effect of H₂O accelerates the formation of CO₂ and N₂. The weak negative oxygen balance of PETN determines that a small amount of CO and H₂ will occur during the thermal instability phase. In the thermal instability stage, there are fewer products with relative molecular weight close to or exceeding PETN, only occupying less than 1% of the total weight fraction, while the proportion of small molecular products is as high as 78%, and some intermediates with relative molecular weight in [75,225] take up about 21%. Rapid and complex reaction events make it difficult for existing experimental and computational methods to accurately predict the structure of these intermediates, which will be the focus of the future research. In conclusion, the research of this paper can provide some reference for the problems, such as ignition of hot spot and ignition-induced deflagration and detonation of energetic materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03133.
Effect of thermal duration on ignition of PETN crystal when the temperature of chemical reaction center region is 1000 K (PDF)

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Notes
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