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**Mechanisms and kinetics of initial pyrolysis and combustion reactions of
1,1-diamino-2,2-dinitroethylene from density functional tight-binding molecular
dynamics simulations**

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Abstract : Density functional tight-binding molecular dynamics was used to study the mechanisms and kinetics of initial pyrolysis and combustion reactions of isolated and multimolecular FOX-7. Based on the thermal cleavage of bridge bonds, the pyrolysis process of FOX-7 can be divided into three stages. However, the combustion process can be divided into five decomposition stages, which is much more complex than the pyrolysis reactions. The vibrations in the mean temperature contain nodes signifying the formation of new products and thereby the transitions between the various stages in the pyrolysis and combustion processes. Activation energy and pre-exponential factor for the pyrolysis and combustion reactions of FOX-7 were obtained from the kinetic analysis. It is found that the activation energy of its pyrolysis and combustion reactions are very low, making both of them take place fast. Our simulations provide a first atomic-level look at the full dynamics of the complicated pyrolysis and combustion process of FOX-7.

Key words: Pyrolysis and combustion reactions, FOX-7, Activation energy, Pre-exponential factor

Introduction

1,1-diamino-2,2-dinitroethylene (FOX-7; Figure 1a) is a high energy compound with low sensitivity in nature, which represents a nitroamine class of energetic compounds.¹⁻³ The low sensitivity of FOX-7 is attributed to strong two-dimensional hydrogen bonded network²⁻⁶ that are similar to that in a known insensitive explosive TATB (triaminotrinitrobenzene).^{7,8} Since the FOX-7 was synthesized in 1998,⁹ many studies have carried out on its synthesis, mechanism, molecule structure, thermal behavior, detonation performance, and application.^{2,3,7,9-13} Recently, FOX-7 has been successfully applied to synthesizes closed-loop derivatives of the explosives.¹⁴⁻¹⁵ For example, Shreeve et al¹⁴ reported several energetic ionic salts containing two FOX-7-derived anions: 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion and dianion. Sun et al¹⁵ synthesized five disubstituted closed-loop derivatives of FOX-7 and some properties were reported in succession. These closed-loop derivatives of FOX-7 have excellent detonation performance due to their fair similar structure to diazo FOX-7. The crystal structure and behaviors of condensed phase FOX-7 under low-pressure,^{16,17} low-temperature,^{18,19} and high-pressures^{20,21} were successfully studied using density functional theory (DFT). This is very important to understand their complicated behaviors and control their risk during usage and storage.

< Figure 1 about here >

Although many studies have centered on FOX-7, the full microscopic pictures of initiation pyrolysis and combustion mechanisms of the FOX-7 remain unclear. Molecular dynamics simulation has been proven to be an effective and economical

way to investigate the reaction and combustion behaviors under extreme conditions. Among molecular dynamics simulations,²²⁻²⁸ the density functional tight-binding (DFTB) molecular dynamics (MD) simulations have been widely used for studying the pyrolysis mechanisms of the explosives.²⁹⁻³⁰ The decomposition behaviors of TATB, whose structure is similar to FOX-7, were studied under different temperatures³¹⁻³⁷ or temperature coupled with different pressures.²⁵ However, there are few researches on the pyrolysis mechanisms of FOX-7. Recently, the detailed insight of the key reactive events related pyrolysis and combustion of hydrogen,³⁸ biomass particle,³⁹ and several fuels⁴⁰⁻⁴⁴ were reported by MD simulations. These studies facilitate our understanding of comprehensive combustion chemistry. Therefore, a computationally feasible atomistic tool can be used to simulate the chemistry and physics involved in complex combustion processes of the explosives.

In this work, we performed DFTB-MD simulations to study the initial pyrolysis and combustion reaction mechanisms and kinetics of unimolecular and multimolecular FOX-7 at high temperatures. Our main purpose here is to (1) understand the clear atomic picture of pyrolysis and combustion of FOX-7; (2) to determine the kinetic parameters of FOX-7 for pyrolysis and combustion. Our studies are helpful for understanding the chemical mechanisms underlying the pyrolysis and combustion of the explosives.

Computational methodology

DFTB-MD simulations

Static calculations were performed using third-order corrected self-consistent

charge density-functional tight-binding method (SCC-DFTB) ⁴⁵ implemented in the DFTB+ code.⁴⁶ We optimized the geometry of FOX-7 in a box with period boundary conditions to model the thermal decomposition confined within a relatively free space. The SCC tolerance was set to 10^{-5} au. The conjugate gradient method (CG) was used for the cell optimization. The convergence criteria for the maximum geometry change was less than 3.0×10^{-3} bohr, the maximum force component was less than 4.5×10^{-4} hartree/bohr, the root-mean-square geometry change was less than 1.5×10^{-3} bohr, and the root-mean-square force was less than 3.0×10^{-4} hartree/bohr.

DFTB-MD simulations were performed on the FOX-7 systems under constant energy and volume conditions (NVE ensemble) ⁴⁷ with a 1 fs time step. The pyrolysis and combustion temperature was set to be the flame temperature (T_f) of 2799 K.² To identify the concentration of stable molecular species, the chemical species were defined based upon a set of bond-distance cutoff criteria ⁴⁸ in this work. Two atoms were not considered to be bonded unless they stayed continuously within the bond-distance criteria during the minimum bond lifetime of 25 fs.⁴⁹⁻⁵² We used a larger bond lifetime of 45 ps to identify stable molecular species. It is found that the time evolution of the species identified by the larger bond-distance criteria had no effect on the qualitative conclusions in this work. Thus, the chemical reaction events and kinetic parameters were traced by the concentrations of the species.

Simulation parameters

Pyrolysis simulations parameters

The unimolecular pyrolysis simulations were performed on a single FOX-7

(Figure 1b) molecule in a cubic periodic cell with sides of 16 Å using NVE ensemble dynamics. The density of the system is 0.06 g/cm³. To do that, first, we minimized the system and then the system was equilibrated for 15 ps at 298.15 K by NVT-MD simulation with a 1 fs time step. The thermostat was used to control the temperature. After this equilibration, we chose 10 independent starting configurations at 2799 K and performed 10 parallel independent NVE-MD simulations for 50 ps.

For multimolecular pyrolysis simulations, the modelling conditions were the same as those for the unimolecular case. 50 FOX-7 molecules (Figure 1c) were put into a periodic cubic box with sides of 62.65 Å to achieve the same density as used in the unimolecular model. The density of the system is 0.05 g/cm³. The system was first equilibrated at 298.15 K for 15 ps with a time step of 1 fs and then was heated to 2799 K. Then, we carried out MD simulations for another 50 ps at 2799 K with a time step of 1 fs.

In addition, to verify the size dependence of the system, we performed one additional large-scale simulation with a larger cubic box with sides of 70.08 Å with the same density 0.05 g/cm³ (Figure 1d) at 2799 K for 15 ps with a 1.0 fs time step after the system was equilibrated at 298.15 K for 15 ps.

Combustion simulation parameters

To study the detailed initial combustion mechanisms, we first simulated a unimolecular model. We placed a single FOX-7 molecule in a cubic periodic box with 16 Å sides and added 2 oxygen molecules (Figure 1e) leading to an equivalent ratio of $\Phi \approx 1.0$ and a density of 0.07 g/cm³. The system was first equilibrated at 298.15 K for

15 ps with a 1 fs time step and heated to 2799 K for 50 ps with a 1 fs time step in the NVE ensemble. In the equilibrium and heating processes, the bond interactions between (C, H) and O were turned off to prevent combustion reactions from occurring. Again, 10 parallel independent simulations were carried out to provide proper statistics and the opportunity for a variety of mechanisms to occur.

For multimolecular combustion simulations, we put 50 FOX-7 molecules and 100 oxygen molecules into a cubic box of 62.93 Å sides length (Figure 1f). This leads to an equivalent ratio of $\Phi \approx 1.0$ and the 0.06 g/cm³ density. The box was first equilibrated at 298.15 K for 15 ps with a 1 fs time step and heated to 2799 K in 50 ps with a 1 fs time step using the NVE ensemble.

Kinetic analysis of pyrolysis and combustion reactions

To investigate the kinetic properties for pyrolysis and combustion, we carried out NVE-MD simulations on the multimolecular models for several temperatures. We considered the range of 2779-2819 K in 10 K steps for the pyrolysis and combustion simulations to obtain kinetic analysis. These simulations were carried out for 50 ps (50000 trajectories) at each temperature with a 1 fs time step for the pyrolysis and the combustion models. Firstly, we counted the numbers of the unreacted FOX-7 in the initial pyrolysis and combustion during the simulated reaction time to obtain the initial loss rate of the reaction molecules. Secondly, the Arrhenius plots of apparent first-order rate constants for both the multimolecular pyrolysis and combustion reactions of FOX-7 were drawn. Thirdly, their activation energy $E_a(\text{pyr})$ and the pre-exponential factor A were obtained by the Arrhenius plots.

Results and discussion

Pyrolysis

Unimolecular pyrolysis

It was found in Figure 2 that the initial decomposition of FOX-7 was triggered by the unimolecular breaking of N-O bond from 10 parallel simulations.

< Figure 2 about here >

FOX-7 possesses the same nitro- and amino- structure as TATB, which is an outstanding representative of insensitive explosives. Many experiments proposed four distinct reactions in the thermal decomposition of TATB like the C-NO₂ bond rupture,³¹ carbon ring dissociation,³² C-NH₂ bond cleavage,³³ and hydrogen transfer^{34,25} and identified some key decomposition intermediates (INTs) and gas products. However, these are different from the initial decomposition reaction of the N-O bond cleavage for the FOX-7 molecule studied herein. Zhu et al.⁵³ reported that the initial decomposition of shocked HMX was triggered by the N-O bond breaking and the ring opening. This indicates that the initial mechanism by the N-O bond cleavage for the nitro explosives is probable.

Figure 3 displays a schematic diagram of the competing unimolecular pyrolysis channels for subsequent decomposition paths of unimolecular FOX-7 during ten parallel simulations. Compared with path (2), the appearance incidence of path (1) is predominant for nine out of ten. Therefore, the N-O fission predominates in the secondary thermal decomposition stages of the FOX-7 molecule. More detailed subsequent decomposition processes that took place after the secondary

decomposition reactions are also shown in Figure 3. After the N-O bond cleavage, INT1 decomposed accompanied by the cleavage of the C-C and C-N bonds to form oxygen radicals and release NO. Most of the intermediate products are very unstable. For example, one FOX-7 molecule rapidly decomposed into one NO molecule, two oxygen radicals, and one heterocyclic radical. The heterocyclic radical further decomposed to form $\text{H}_2\text{NC}\equiv\text{CNH}_2$ fragment and other NO molecule. Some small intermediates decomposed in a stepwise manner to produce HCN molecule or H_2NCHO .

< Figure 3 about here >

INT1 is an intermediate produced directly from the N-O bond cleavage, which is considered as “stage I”. This stage occurred in the reaction time range from 0 to 9 ps, where is the first node of the mean temperature vibration (Figure 4). The corresponding intermediates were observed at the simulation reaction time when the node appeared. The time-dependent mean temperature was averaged over 10 trajectories. When the reaction time increases to 9-25 ps, it is the second stage of the pyrolysis (stage-II). Meanwhile, the second node area of the mean temperature values appears. INT1 began to crack into $\text{H}_2\text{NC}\equiv\text{CNH}_2$ fragment and produced many unstable heterocyclic compounds along with a small fraction of oxygen radicals and NO gases. Furthermore, the produced radicals and gas can be used as an indicator for the pyrolysis stage transitions, namely from $\text{H}_2\text{NC}\equiv\text{CNH}_2$ to stage-II. The last pyrolysis stage (stage-III) began after 25 ps, which is characterized by further decomposition of $\text{H}_2\text{NC}\equiv\text{CNH}_2$ into small OH, NO, and $\cdot\text{C}=\text{NH}$ radicals. The

amounts of large fragment ($\text{H}_2\text{NC}\equiv\text{CNH}_2$) reaches their minimum, while those of small radicals ($\cdot\text{C}=\text{NH} + \text{OH}$) and gases (NO) keep growing with the reaction time. Therefore, the pyrolysis process of FOX-7 can be divided into three stages on the basis of the evolution profile of products in weight percentage and the mean temperature values with reaction time: the first node for initial decomposition stage and the second node for forming the small radicals and gas radicals.

< Figure 4 about here >

Multimolecular pyrolysis

For multimolecular pyrolysis simulations, the thermal conditions were the same as those for the unimolecular model. It is found that the initial decomposition is triggered by the unimolecular cleavage of the N-O bond to form an oxygen radical just like that of the isolated FOX-7. We observed three different decomposition channels for the pyrolysis of the 50 FOX-7 molecules, as shown in Table 1.

It is seen in Table 1 that the reaction path R1 is as follows: the initial reaction R1 involves the N-O bond cleavage to form a biradical intermediate, which then transfers oxygen radicals to form more stable intermediates. This was observed 36 times for the 50 FOX-7 molecules. The reaction path R2 is as follows: the initial reaction R2 happened by the N-H bond breaking to form a biradical intermediate, which then transfers a hydrogen atom to accelerate the following reactions. This was observed 11 times for the 50 FOX-7 molecules. The reaction path R3 is as follows: three FOX-7 molecules are triggered by the breaking of C-C bond. This reaction channel has relatively lower possibility than the reaction R1 and R2. The biradical intermediate

are very active to accelerate the following complex reactions. In all, during both the unimolecular and multimolecular pyrolysis, the N-O bond cleavage is a main reaction channel.

< Table 1 about here >

In addition, to verify the size dependence of the system, we performed one additional large-scale simulation with a large supercell with 70 FOX-7 molecules. It is found that the decomposition channels of FOX-7 with the large model are nearly the same as those with the small model. Among the 70 FOX-7 molecules, 49 molecules were observed to decompose by the N-O breaking. Therefore, the N-O cleavage is a main decomposition channel of the FOX-7 crystal. 19 FOX-7 molecules decomposed by the breaking of N-H bond. Only two FOX-7 molecules reacted through channel R3 by the cleavage of C-C bond. The ratio of every channel is nearly the same as that for the small model with 50 FOX-7 molecules. It demonstrates that the size of the small supercell containing 50 FOX-7 molecules is large enough for studying the decomposition of FOX-7 system.

Figure 5 presents the time evolution of the numbers of the main fragments during the decomposition of the FOX-7 crystal. The numbers of the fragments were calculated by averaging over 10 trajectories. At about 200 fs, one NO₂ molecule was released by the breaking of the C-NO₂ bond. However, NO₂ broke to produce other small fragments and disappeared at 1300 fs. The numbers of hydrogen radicals vibrate sharply. This may be caused by the light and mobile character of the hydrogen radical, which is similar to that described in previous reports, such as studies on the thermal

decompositions of PETN ⁵² and crystalline furoxan.⁵⁴ The formation of molecular nitric oxide was found to be delayed for 200 fs. The main decomposition products of the FOX-7 crystal are oxygen radicals, hydrogen radicals, and nitric oxide derivatives.

< Figure 5 about here >

Oxidation

Unimolecular combustion

10 parallel independent simulations were carried out to provide proper statistics and the opportunity for a variety of mechanisms to occur. It is found that the initial decomposition step of FOX-7 is triggered by the unimolecular N-O bond breaking (Figure 6). The initiation combustion mechanism is similar to that described in previous initiation pyrolysis mechanism. The generated isolated oxygen radical is much more active in the oxygen-rich environment and can promote further reactions. The oxygen radical transfers to attack C=C bond and form cyclopropanone by forming two new C-O bonds. The results display that the oxygen does not participate in the reaction directly, but it affects subsequent reactions of other radicals. The oxygen-rich environment accelerates further decomposition reactions that are much different from the unimolecular pyrolysis of FOX-7.

< Figure 6 about here >

Figure 7 presents competing decomposition channels for subsequent combustion reactions of a single FOX-7 molecule obtained from ten parallel simulations. It is found that there are four major distinctive channels for the decomposition of the intermediate INT2'. They include: (1) INT2' decomposed by the C-NO bond cleavage

to release NO. This was observed 5 times in our 10 independent simulations; (2) INT2' decomposed by the N-O bond breaking to form oxygen radical. This was observed 3 times in our 10 independent simulations; (3) the C-NO₂ bond of INT2' opened to release NO₂. This was observed only 1 time in our 10 independent simulations; (4) INT2' decomposed by the N-H bond breaking. This was observed only 1 time in our 10 independent simulations. The combustion process is much more complex than that of the pyrolysis.

< Figure 7 about here >

Compared with other reaction channels, the C-NO bond fission predominates in the early combustion decomposition stages of FOX-7. This indicates that the C-NO bond fission is a new decomposition mechanism for the combustion processes of FOX-7. The channel of the N-O bond rupture during the combustion of FOX-7 is similar to that described in previous reports on the thermal decompositions of HMX.⁵³ However, the probability of this pathway is low compared with main pyrolysis paths because the oxygen-rich environment could decelerate the formation of oxygen radicals. The combustion mechanisms (3) and (4) of FOX-7 are much more similar with several ignition mechanism like the C-NO₂ bond dissociation³⁴ and the N-H bond breaking.²⁵ However, the possibility of the two pathways are very low since the first two channels make up a large majority (>80%) of the 10 parallel independent simulations.

Figure 8 shows mean temperature vibration of the unimolecular combustion of FOX-7 with time evolution. The time-dependent mean temperature was averaged over

10 trajectories. During the whole reaction process, there are four nodes that separate the reaction stage to five sections. An investigation of the concentrations of the radicals and the mean temperature vibration together with the reaction details described in Figure 7 suggests that temperature nodes and major pyrolyzates can be used as the indicators of the combustion stage transitions. The first pyrolysis stage (stage-I) occurs for the first node during the stage from 0 to 8 ps, where the INT2' is the combustion products obtained directly by the oxygen radicals attacking C=C bond to form one heterocyclic radical. This step may be the main differences between the combustion and pyrolysis decomposition mechanisms. When the reaction time is during 8-15 ps, the radical INT2'-2 appears in the second pyrolysis stage (stage-II). The subsequent decomposition processes are accompanied by the cleavage of the C-N and N-O bonds to release NO and form various types of radicals. The stage-III occurs from 15 to 23 ps. The fragment INT2'-4 formed by the complex INT2'-2, which opened the C-NO bond to form several radicals; most of the radicals are very unstable. Oxygen attacked the carbonyl to form INT2'-4 and oxygen radicals. This is the direct participation step of oxygen in the combustion reaction. The fourth stage "stage IV" continued from 23 to 33 ps. INT2'-4 decomposed to form $(\text{H}_2\text{N})_2\text{C}=\text{C}=\text{O}$ fragment along with a small fraction of oxygen radicals and NO gas. The last stage is that the intermediate decomposed to form $\cdot\text{C}(\text{NH}_2)_2$, oxygen radicals, CO, and NO. Although our simulations were performed on an isolated FOX-7, the results provided an important qualitative picture for understanding its combustion decomposition.

< Figure 8 about here >

Multimolecular combustion

The combustion reactions of the multimolecular system are more complex than those of the unimolecular system. The initial combustion mechanism of the FOX-7 multimolecular system is the cleavage of one oxygen molecule to form two oxygen radicals, occurred at first 10 fs. It is found that the decomposition of FOX-7 is triggered by the N-O bond breaking. In all, the DFTB-MD simulations predicted that the decomposition mechanisms of the 50 FOX-7 molecules include four competition reaction channels: the cleavage of N-O bond (channel 1); the N-H bond breaking (channel 2); the C-C bond rupture (channel 3); intramolecular hydrogen transfer (channel 4). The typical reaction pathways of the competing channels are illustrated in Table 2.

< Table 2 about here >

The first two channels make up a large majority (>99%) of the overall channels from the 50 independent trajectories. For example, the major initial reaction channel of FOX-7 is channel 1. This was observed 36 times for our 50 FOX-7 molecules. The predominance of channel 1 in the combustion of FOX-7 is consistent with the conclusions from its multimolecular pyrolysis. The cleavage of N-H bond to release hydrogen radicals was observed 12 times. This channel is another governed reaction process. This triggering mechanism is the same as initial thermal decomposition step of crystal dihydrazinium 3,3'-dinitro-5,5'-bis-1,2,4-triazole-1,1-diolate.⁵⁵ The hydrogen radicals would accelerate subsequent reactions, in agreement with previous studies on the thermal decompositions of PETN,⁵² crystalline furoxan,⁵⁴ and TEX.⁵⁶

The total occurrence numbers of channel 1 and channel 2 in the combustion of FOX-7 is the same as those in its pyrolysis process. Channel 3 occurred only one time. The occurrence probability of channel 3 is much less than that in the multimolecular pyrolysis of FOX-7. Channel 4 also took place one time. The initial decomposition step was found to be the intramolecular hydrogen transfer to form O-H bond. The transfer behavior of the hydrogen is similar to previous report on the thermal decomposition of TATB.²⁵ This channel was just observed in the multimolecular combustion of FOX-7, but not in its unimolecular combustion.

Figure 9 presents the time evolution of the numbers of the reactants FOX-7 and O₂ and intermediates NO₂, O, NO, and H during the multimolecular combustion of FOX-7 at 2799 K. The numbers of the reactants and intermediates were averaged over 10 trajectories. The reaction of the reactant FOX-7 with O₂ completed at 1.8 ps. The radicals OH, NO, NO₂ and H reach the equilibrium numbers of 1, 2, 4 and 12, respectively. The numbers of oxygen radicals increase as the reaction continues. The equilibrium numbers of the H and oxygen radicals are much higher than that of the OH fragment. The primary products during the combustion of FOX-7 are O, H, and various nitrous oxide derivatives.

< Figure 9 about here >

Kinetic analysis of pyrolysis and combustion

Our MD simulations on the multimolecular pyrolysis and combustion of FOX-7 can investigate the reaction kinetic properties at several temperatures. The flame temperature of 2779 K was used for both pyrolysis and combustion of FOX-7.

Moreover, the 10 K step from 2799 K to 2819 K was adopted for the kinetic models of pyrolysis and combustion. These simulations were carried out by using a time step of 1 fs at each temperature for 50 ps.

Figure 10 displays the Arrhenius plots of the apparent first-order rate constants for both the pyrolysis and combustion reactions of FOX-7. The activation energy $E_a(\text{pyr})$ for the pyrolysis of FOX-7 is 11.31 kcal/mol. The pre-exponential factor derived from the pyrolysis simulations is $A = 3.418 \times 10^{12}$. Transition state theory leads to $k = (k_B T/h) \exp(\Delta S^\ddagger/R)$, where $\Delta S^\ddagger = -251.08$ J/mol/K. Also, the activation energy $E_a(\text{comb})$ for the combustion of FOX-7 is 8.15 kcal/mol with a pre-exponential factor of $A = 3.82 \times 10^{11}$. The activation entropies $\Delta^\ddagger S$ were calculated from the Eyring equation to be -257.65 J/mol/K. The negative activation of entropy suggests that both the pyrolysis and combustion reactions conduct in a bimolecular mechanism. Therefore, the combustion reactions of FOX-7 have lower E_a and k than the pyrolysis because O_2 can accelerate initial bond breaking step but decelerate the activation energy of the reaction. Our conclusions are consistent with other ReaxFF studies on the pyrolysis and combustion of 1,6-dicyclopropane-2,4-hexyne that the E_a and k values of the combustion reactions decrease due to the effects of O_2 .⁴⁴

< Figure 10 about here >

Conclusions

In this study, DFTB-MD simulations were performed to study initial pyrolysis and combustion reaction mechanisms and kinetics of isolated FOX-7 molecule and its multimolecular assembly at flame temperature. The results indicate that the initial

decomposition step of isolated FOX-7 is triggered by the unimolecular N-O bond breaking. The decomposition of the multimolecular FOX-7 systems involves three decomposition channels: (a) the N-O bond cleavage to release oxygen radical; (b) the N-H bond breaking; (c) the C-C bond rupture. After the decomposition of the FOX-7 crystal was triggered, some radicals and gas were formed, such as hydrogen radicals and oxynitride.

The combustion decomposition of the isolated FOX-7 molecule is triggered by the unimolecular N-O bond breaking to form oxygen radical. The generated O radical can attack the C=C bond to form three-membered heterocycle. This entropy-driven combustion starts from unimolecular oxidation, generating many radical species, and leading to explosive combustion. In this process, oxygen serves both as a radical acceptor and as a radical producer, which dramatically increases the combustion rates. Major products observed in the simulations include NO₂, NO, H, and O etc. An ene-carbonyl compound was generated from the radical reaction by attacking the cyclopropane ring. The combustion decomposition of the multi FOX-7 molecules is triggered by the O-O bond breaking to form two oxygen radicals. Subsequent reactions include four competition reaction channels: the N-O bond cleavage (channel 1); the N-H bond breaking (channel 2); the C-C bond rupture (channel 3); intramolecular hydrogen transfer (channel 4).

Furthermore, the activation energy of its pyrolysis and combustion reactions are found to be very low, making both of them take place fast.

Our study may provide new insight into understanding the initial pyrolysis and

combustion mechanisms of FOX-7 under flame temperature in atomic detail.

Acknowledgments

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Table 1. Initial decomposition paths in the multimolecular pyrolysis of FOX-7.

Table 2. Initial decomposition paths in the multimolecular combustion of FOX-7.

Figure 1. Molecular structure of a single FOX-7 molecule (a), a cubic periodic cell with a single FOX-7 molecule (b), a periodic cubic box with 50 FOX-7 molecules (c), a periodic cubic box with 70 FOX-7 molecules (d), and a cubic periodic box with a single FOX-7 molecule and 2 oxygen molecules (e), and a cubic periodic box with 50 FOX-7 molecules and 100 oxygen molecules (f); Gray, blue, red, and white spheres stand for carbon, nitrogen, oxygen, and hydrogen atoms, respectively.

Figure 2. Initial decomposition mechanism for the unimolecular pyrolysis of FOX-7 under flame temperature 2799 K. The first stage of unimolecular pyrolysis obtained from ten parallel simulations.

Figure 3. Competing decomposition channels for subsequent pyrolysis reactions of a single FOX-7 molecule at 2799 K obtained from ten parallel simulations.

Figure 4. Mean temperature vibration of the unimolecular pyrolysis of the FOX-7 molecules with time evolution from ten parallel unimolecular simulations. Linkage consumption in the three stages of unimolecular pyrolysis according with mean temperature vibration.

Figure 5. Time evolution of the numbers of the reactant FOX-7 and intermediates NO_2 , O, NO, and H at 2799 K. The spline trendlines correspond to the actual concentration data of the matching color behind.

Figure 6. Initial combustion decomposition mechanism for a single FOX-7 molecule at 2799 K from ten parallel simulations.

Figure 7. A schematic diagram of the competing unimolecular combustion

decomposition channels of ten times simulation for the following reactions unimolecular FOX-7 molecule under the flame temperature 2799 K. The following four stages of unimolecular combustion obtained from the ten parallel simulations.

Figure 8. Mean temperature vibration of the unimolecular combustion of FOX-7 with time evolution. Linkage consumption in the five stages of unimolecular combustion according with mean temperature vibration.

Figure 9. Time evolution of the numbers of the reactants FOX-7 and O₂ and intermediates NO₂, O, NO, and H at 2799K. The spline trendlines correspond to the actual concentration data of the matching color behind.

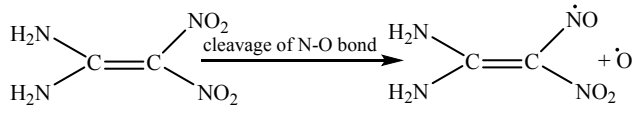
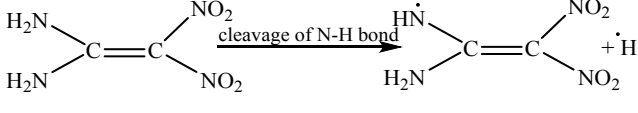
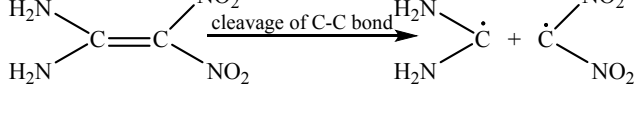
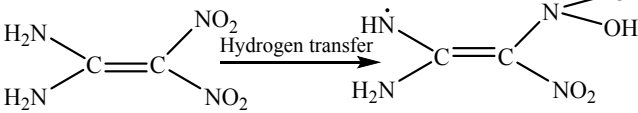
Figure 10. Arrhenius plots of apparent first-order rate constants for both the multimolecular pyrolysis and combustion reactions of FOX-7. Black is for the pyrolysis and red is for the combustion.

Table 1. Initial decomposition Paths in the Multimolecular Pyrolysis of FOX-7

Reaction	Reactions	Times observed
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Paths		50FOX-7	70FOX-7
R1	$ \begin{array}{c} \text{H}_2\text{N} \quad \text{NO}_2 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_2\text{N} \quad \text{NO}_2 \end{array} \xrightarrow{\text{cleavage of N-O bond}} \begin{array}{c} \text{H}_2\text{N} \quad \dot{\text{N}}\text{O} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_2\text{N} \quad \text{NO}_2 \end{array} + \dot{\text{O}} $	36	49
R2	$ \begin{array}{c} \text{H}_2\text{N} \quad \text{NO}_2 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_2\text{N} \quad \text{NO}_2 \end{array} \xrightarrow{\text{cleavage of N-H bond}} \begin{array}{c} \text{HN} \quad \text{NO}_2 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_2\text{N} \quad \text{NO}_2 \end{array} + \text{H} $	11	19
R3	$ \begin{array}{c} \text{H}_2\text{N} \quad \text{NO}_2 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_2\text{N} \quad \text{NO}_2 \end{array} \xrightarrow{\text{cleavage of C-C bond}} \begin{array}{c} \text{H}_2\text{N} \quad \dot{\text{C}} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_2\text{N} \quad \text{NO}_2 \end{array} + \dot{\text{C}} \begin{array}{c} \text{NO}_2 \\ \diagdown \quad / \\ \text{NO}_2 \end{array} $	3	2

Table 2. Initial decomposition Paths in the Multimolecular Combustion of FOX-7

Reaction Paths	Reactions	Times observed
R1		36
R2		12
R3		1
R4		1

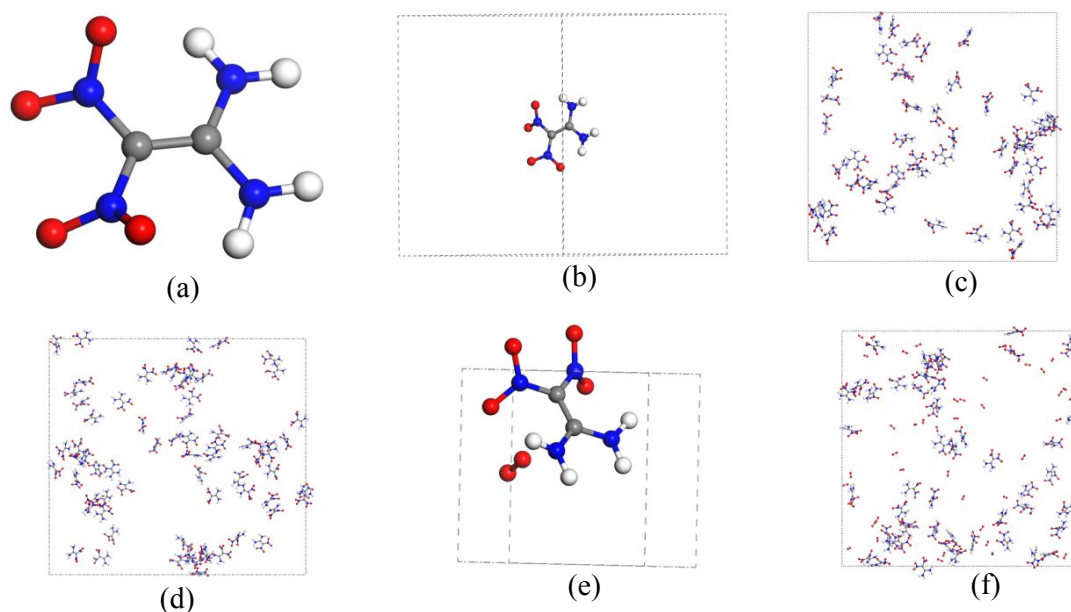


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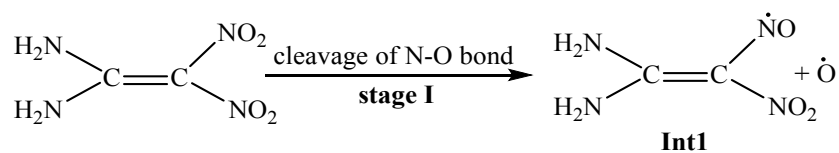
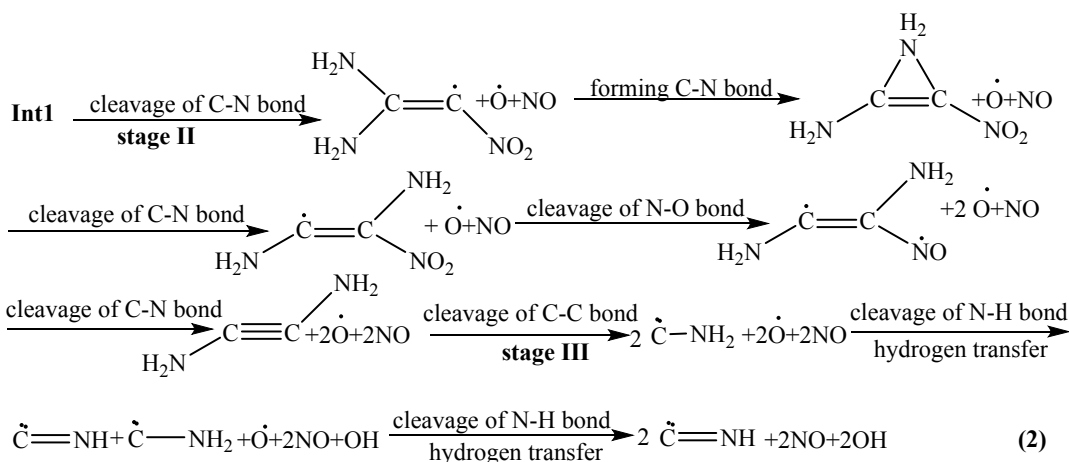


Figure 2. Initial decomposition mechanism for the unimolecular pyrolysis of FOX-7 under flame temperature 2799 K. The first stage of unimolecular pyrolysis obtained from ten parallel simulations.



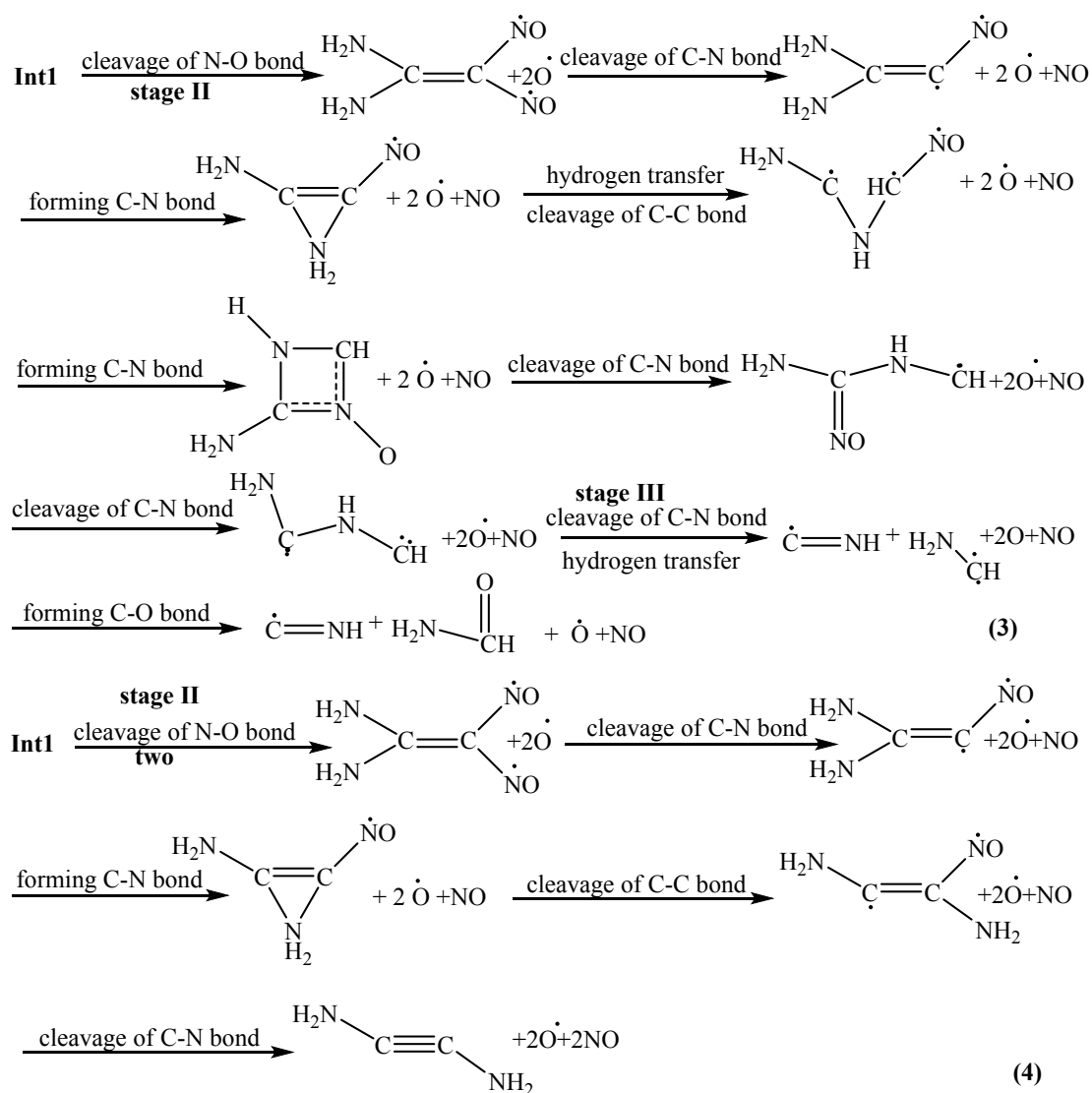


Figure 3. Competing decomposition channels for subsequent pyrolysis reactions of a single FOX-7 molecule at 2799 K obtained from ten parallel simulations.

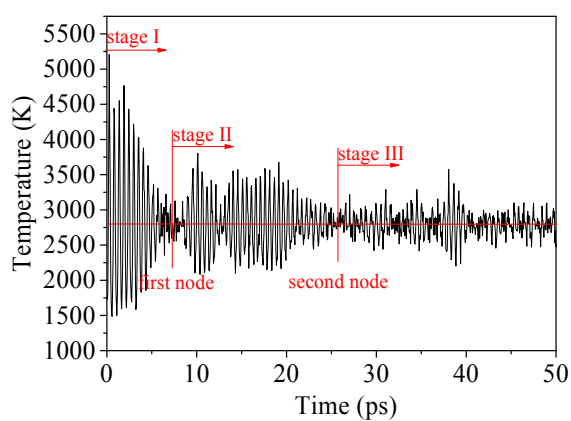


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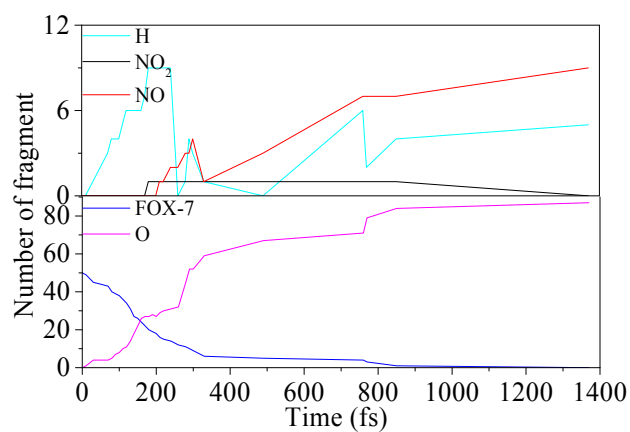


Figure 5. Time evolution of the numbers of the reactant FOX-7 and intermediates NO₂, O, NO, and H at 2799 K. The spline trendlines correspond to the actual concentration data of the matching color behind.

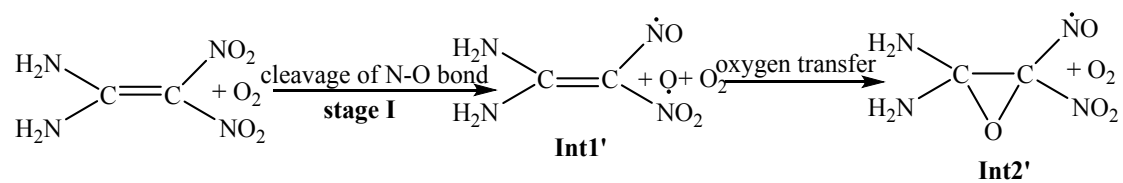


Figure 6. Initial combustion decomposition mechanism for a single FOX-7 molecule at 2799 K from ten parallel simulations.

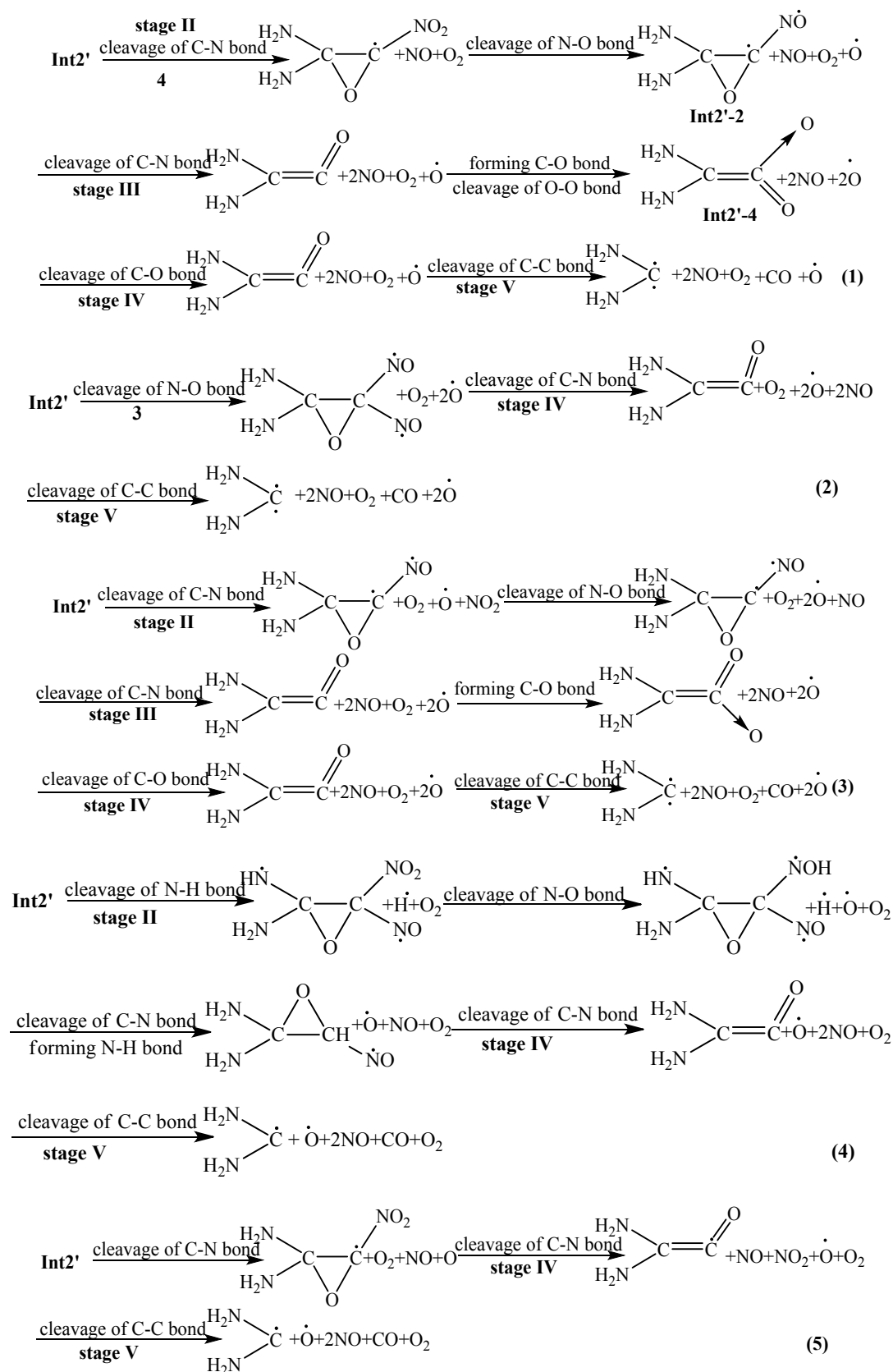


Figure 7. A schematic diagram of the competing unimolecular combustion decomposition channels of ten times simulation for the following reactions

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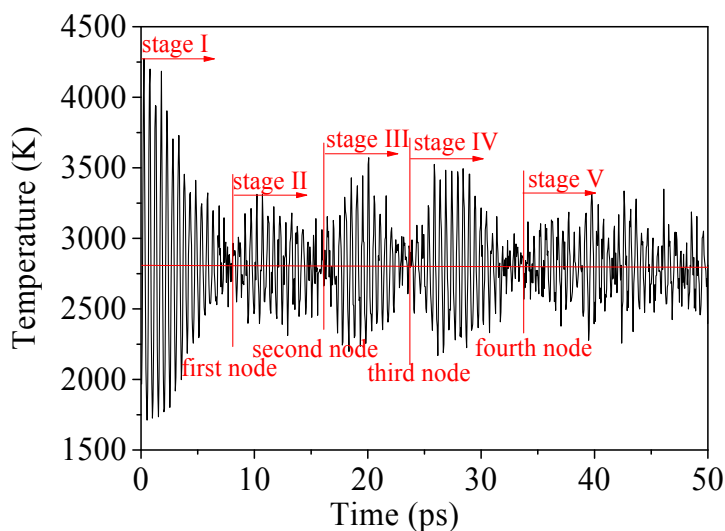


Figure 8. Mean temperature vibration of the unimolecular combustion of FOX-7 with time evolution. Linkage consumption in the five stages of unimolecular combustion according with mean temperature vibration.

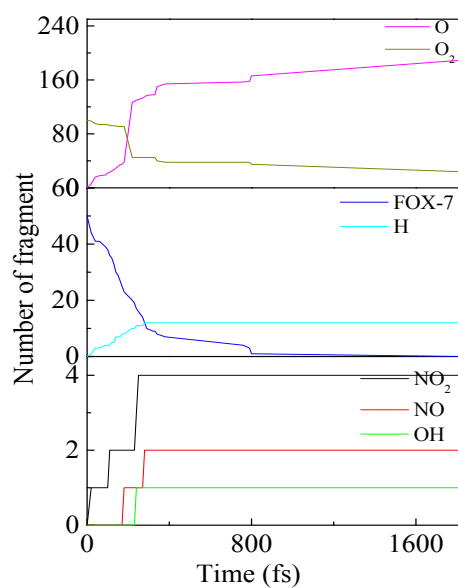


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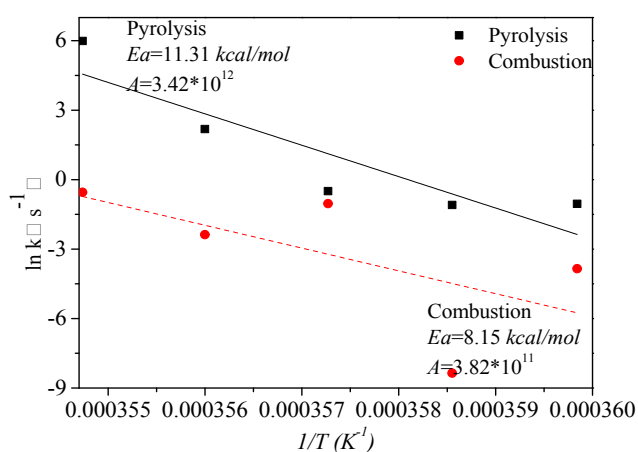


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