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[Huaiyu Jiang](#), [Qingjie Jiao](#), [Chaoyang Zhang](#)*

Posted Date: 4 July 2023

doi: 10.20944/preprints202307.0197.v1

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Article

Polymorph Dependent Initial Thermal Decay Mechanism of 1,1-Diamino-2,2-Dinitroethylene (FOX-7)

Huaiyu Jiang, ^{†,‡} Qingjie Jiao, [†] and Chaoyang Zhang ^{*,†,§}

[†] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China

[‡] Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), P. O. Box 919-311, Mianyang, Sichuan 621900, China

[§] Beijing Computational Science Research Center, Beijing 100048, China

* Correspondence: chaoyangzhang@caep.cn; Tel: 86-816-2493506

Abstract: A self-consistent charge density-functional tight-binding method combined with molecular dynamics simulations is employed to reveal the effect of polymorph on the thermal decomposition stability of 1,1-Diamino-2,2-Dinitroethylene (FOX-7). Two types of heating, constant temperature heating and temperature-programmed heating, are adopted. Potential evolution indicates that γ -FOX-7 possesses the lowest thermal stability, as it is closer to the decomposition state. Crystal form has an important influence on the thermal decomposition of FOX-7, resulting in different decomposition rates and initial reactions. In general, β - and γ -FOX-7 always decompose more completely than α -FOX-7. This work emphasizes the importance of polymorph dependent initial decay of an energetic polymorphic compound once heated in a volume constrained condition.

Keywords: molecular dynamics; polymorph; thermal decomposition

1. Introduction

Energetic materials are widely used as explosives, propellants and pyrotechnics, as they can work powerfully by rapid release of large quantities of gas and heat. Energetic crystal is the core of energetic materials. That is, almost all properties and performance of an energetic compound can be known by theoretical deduction or modelling. In general, energetic compounds feature organic and energetic molecules can be flexible and stacked in various forms. It roots for the universal polymorphism of energetic compounds. In principle, polymorphic transformation can take place by heating and/or pressure. Thereby, structure and property vary, which significantly influence performance. The polymorph and polymorphic transformation are a key object in studying energetic materials.¹

1,1-Diamino-2,2-dinitroethylene (FOX-7)² is considered as one of the most promising energetic materials because it features both high explosive performance and low impact sensitivity. FOX-7 is polymorphic. Under common conditions, the α -form the most stable; and the most stable form changes to β ³ and γ ⁴ when heated at 386 and 446 K at atmospheric pressure, respectively; and it proceeds to other forms when heated or pressured furtherly.^{5,6} Figure 1 demonstrates the crystal structure of three polymorphs of FOX-7 stabilized under atmospheric pressure, including the α -, β - and γ -forms. The molecular structure of FOX-7 may be described as a push-pull ethylene with two donor amino groups ("head") and two withdrawing nitro groups ("tail") within its molecular framework.⁷ In the α - and β -forms, FOX-7 molecules are packed "head-to-tail" forming wave-shaped layers with extensive intra- and intermolecular hydrogen bonding within the layers and weak van der Waals interactions between the layers, while the molecular stacking of γ -FOX-7 tends to be planar. In fact, many structures and properties of these three polymorphs are different from one another. For example, from α - to β - and γ -forms, the maximal molecular torsion angle changes to 35.6°, 25.6° and

20.2°; the packing density varies from 1.907, 1.825 and 1.900 g/cm³ (measured after annealed at 200 K); the lattice energy changes from 178.1, 172.3 and 175.9 kJ/mol; and the β -formed conformer is the most energetically stable.^{8,9} In addition, the heat induced polymorphic transformation produces more readily stacking structures, partly responsible for the low impact sensitivity of FOX-7.⁸

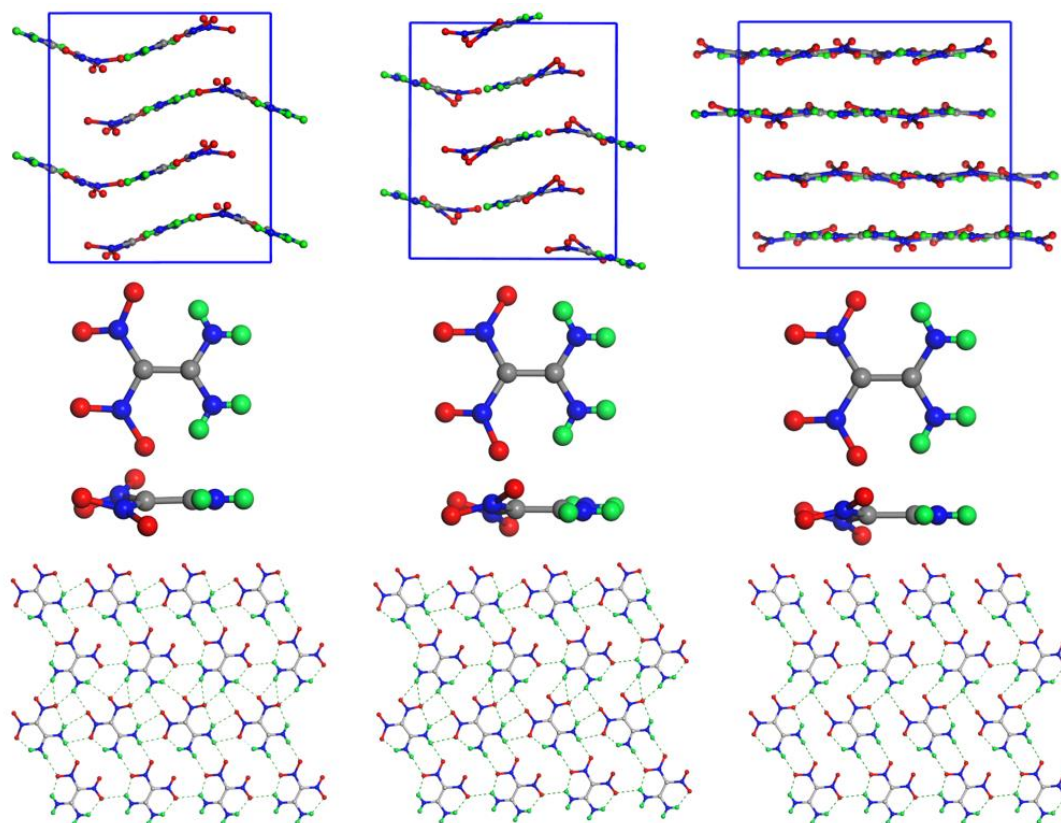


Figure 1. Molecular and stacking structures of the three FOX-7 polymorphs. From top to bottom: molecular stacking structures, molecular structures and intralayered hydrogen bonds represented by green dash.

Besides, the initial thermal decomposition mechanism of FOX-7 attracted much attention, as summarized in Figure 2. The usual HONO elimination, NO₂ loss and NO loss via a nitro-nitrite isomerization in the primary decomposition of nitro molecules¹⁰ are also found in that of α -FOX-7.¹¹⁻¹⁷ In addition, our self-consistent charge density-functional tight binding (SCC-DFTB) molecular dynamics (MD) simulation showed that the N-O bond scission starts the thermal decomposition.¹⁸ Furthermore, two more energetically favored paths, enamino-imino isomerization and intramolecular cyclization, was proposed by Vitaly G. Kiselev and Nina P. Gritsan.¹⁹⁻²¹ On the level of polymorph, Wu et al.²² systematically studied the electronic, optical and thermodynamic properties of the three FOX-7 polymorphs (α , β , and γ -forms) using density functional theory. They found that the N atoms of NH₂ and the C atoms act as active centers and the C-NO₂ fission may trigger the thermal decomposition.

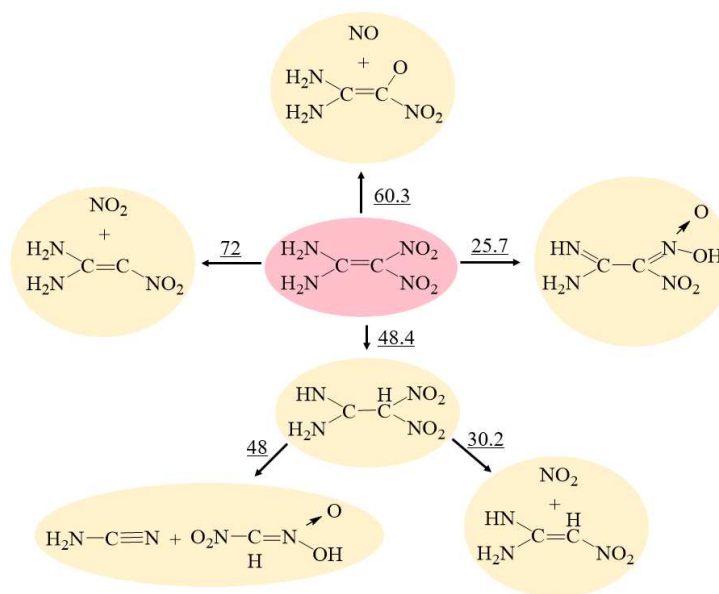


Figure 2. Reported decomposition paths of an isolated FOX-7 molecule.

It is known that the decomposition mechanism of energetic compounds can be polymorph dependent, such as HMX,²³ CL-20²⁴ and RDX.²⁵ To date, there is no polymorph dependent thermal decomposition mechanism of FOX-7 reported. Although the thermal decomposition takes place after the polymorphic transition to the γ -form at atmospheric pressure, the polymorphic transition will not proceed necessarily, for example, if constrained. The study of the change of thermal stability after polymorphic transformation is of great significance for evaluating the applicability of FOX-7. It also provides a basis for assessing the necessity of polymorphic transformation inhibition. In this paper, SCC-DFTB method is employed to reveal the decomposition mechanism of different forms of FOX-7. Thereby, we confirm the decrease of thermal stability of the heat induced polymorph of FOX-7.

2. Methodologies

We employed SCC-DFTB and MD simulation combined method to reveal the thermal decomposition mechanism of the volumetrically constrained three forms of FOX-7. SCC-DFTB is derived from density functional theory (DFT) by approximating interaction integrals.²⁶ It can be seen as an extension of the original non-self-consistent DFTB²⁷ method, which is based on an optimized LCAO basis set and integral approximations. All simulations were performed with 3ob-2-1 potential and DFTB+ 1.3.1 software,²⁸ which was validated to FOX-7 previously.¹⁸

A $2\times 2\times 1$ supercell was constructed to perform MD simulations for each polymorph heated in two styles, constant temperature heating at 1800, 2300 and 3000 K individually, and temperature-programmed heating from 300 to 3000 K with a fixed step of 90 K/ps. All the supercells were first completely relaxed for 500 fs with NVT ensemble, a time step of 0.25 fs and Nose-Hoover thermostat at 300 K. Thereafter, Berendsen thermostat (40 fs damping constant) was used to control the temperature change and the temperature for electron filling was always set to the simulation temperature. The trajectory of each MD simulation was fully recorded per 2 fs, and FindMole procedure²⁹ was employed to analyze the detail of atomic movement. Gamma point was sampled in the Brillouin zone, as the test shows no energy difference between gamma point and $2\times 2\times 2$ k-mesh and a small difference of 0.02 kcal/mol with $3\times 3\times 3$ k-mesh in the energy calculation of α -FOX-7. Obviously, this set facilitates the less time consumption and sufficient presence of reasonable results from the simulations.

3. Results and Discussion

The thermal decomposition of energetic materials always goes through several special stages, such as endothermic stage, exothermic stage and equilibrium stage. The potential energy evolution

analysis facilitates to study the energy response of energetic materials under external stimuli. After relaxed for 500 fs at 300 K, the potential energy of β -FOX-7 and γ -FOX-7 is 3.0 and 6.3 kcal/mol higher than that of α -FOX-7, respectively, suggesting the lowest thermal stability of γ -FOX-7. The potential energy evolution of three forms of FOX-7 under the heating programmed heating from 300 to 3000 K is illustrated in Figure 3d. The potential energy of the three forms is rising steadily at the beginning, followed by a short period of stability, and then starts to decrease. The rise curve represents the endothermic stage, also known as delay interval or induction interval. As can be seen from Figure 3d, γ -FOX-7 first reaches the equilibrium stage and releases energy subsequently, indicating the lowest thermal stability too; while the curves of α -FOX-7 and β -FOX-7 fluctuate.

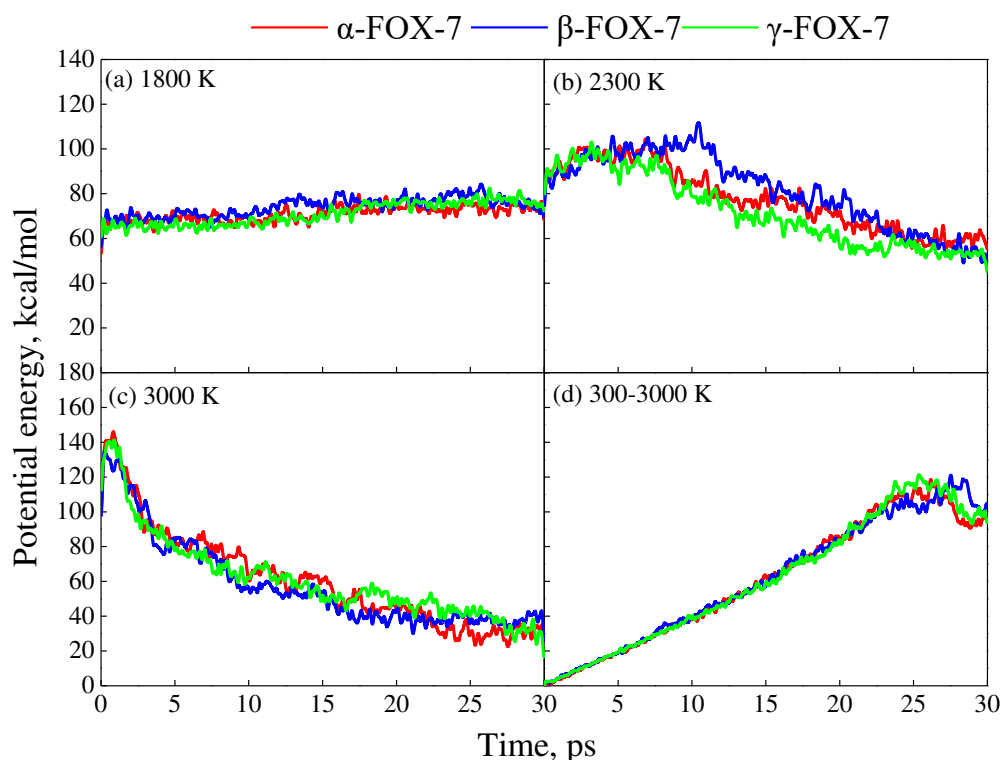


Figure 3. Potential energy evolution of the three FOX-7 polymorphs.

As for constant-temperature heating, three cases of 1800, 2300 and 3000 K are demonstrated in Figure 3a-c. When the temperature is relatively low, the curve of γ -FOX-7 shows a steady and slow rise. At this time, the potential energy curve of α -FOX-7 and β -FOX-7 fluctuates constantly, with a general trend of rising, as shown in Figure 3a. In the case of 2300 K, γ -FOX-7 rapidly accumulates enough potential energy for the next reaction in the first 5 ps. The other two forms start to release energy when the simulation time reaches about 9.5 ps. For the temperature of 3000 K, the potential energy of the three forms immediately reaches to peaks, followed by a reduction; and that of γ -FOX-7 decreases the most rapidly. In general, γ -FOX-7 exhibits the lowest thermal stability at all. In particular, under the condition of constant temperature heating, the endothermic stage of γ -FOX-7 lasts for the smallest time. All these show the lowest thermal stability of γ -FOX-7.

The initial thermal decomposition reactions of energetic materials play an important role in governing thermal stability. Under constant temperature heating at 1800 K, the three forms FOX-7 tend to undergo intramolecular hydrogen transfer first, as shown in Figure 4. Among them, α -FOX-7 presents intramolecular hydrogen transfer at 29.16 ps with a pressure of about 4.25×10^7 Pa. Subsequently, the simulation reaches the upper limit of 30 ps. In the case of β -FOX-7, intramolecular hydrogen transfer occurs at 10.66 ps and the pressure of about 7.09×10^8 Pa. Subsequently, the molecular framework is broken, and the small molecular groups, such as OH and NH₂, are formed and react with the surrounding unreacted FOX-7 molecules. By the end of the simulation, 4 (16 in total) FOX-7 molecules react. As for γ -FOX-7, when the pressure is about 3.20×10^9 Pa at 17.64 ps,

intramolecular hydrogen transfer occurs, with OH and $C_2(NH_2)_2NO_2NO$ generated. OH continues to react with the neighboring FOX-7 molecule and combines one H atom to form H_2O . Finally, only two FOX-7 molecules undergo thermal decomposition. Wholly, the three polymorphs of FOX-7 tend to undergo intramolecular hydrogen transfer first at relatively low temperature, and α -FOX-7 is significantly more stable than β -FOX-7 and γ -FOX-7.

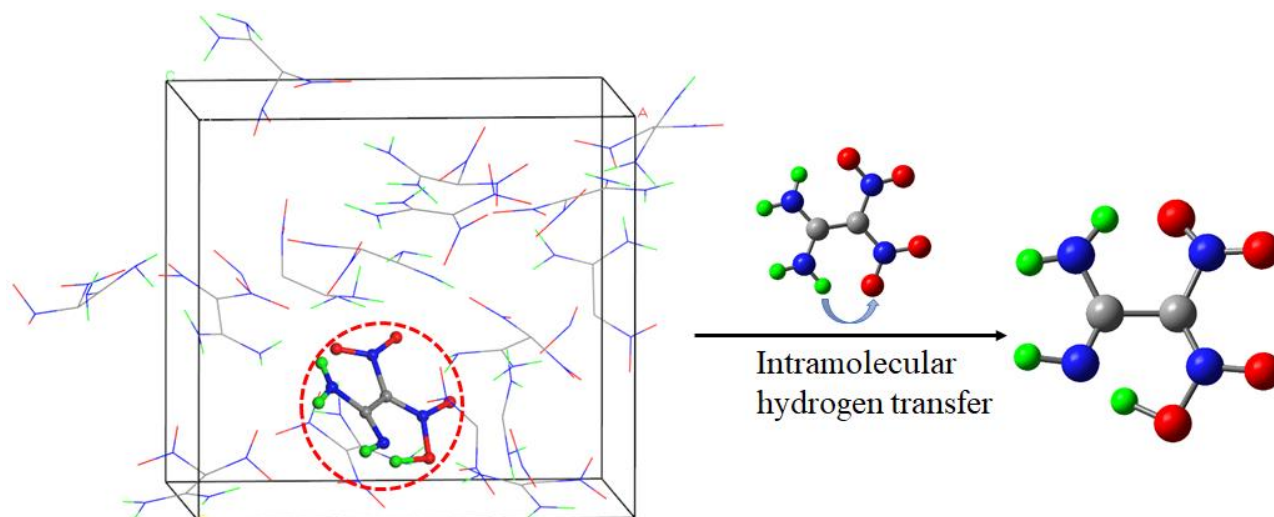


Figure 4. Intramolecular hydrogen transfer in heating α -FOX-7 at 1800 K.

In the MD simulations of 2300, 3000 and 300-3000 K, all the FOX-7 molecules decompose. Two typical reactions occur in each simulation, that is, NO_2 loss and hydrogen loss in reactions with intermediate products. As for the latter one, we find that fragments such as CNO, OH and $(NH_2)_2C=C(NO_2)$, are produced from earlier reactions and do have the ability to capture H atoms from the unreacted FOX-7 molecules. The following analysis deals only with specific types of reactions other than these two. As show in Table 1, in the case of 2300 K, the loss of O atom through reacting with intermediates like H and OH occurs in all of the three forms of FOX-7 (Figure 5). Such reaction occurs once, 4 times and 3 times for α -, β - and γ -FOX-7, respectively. Intramolecular hydrogen transfer, as the initial decomposition step at 1800 K, happens once for β -FOX-7 heated at 2300 K. Another special reaction, intramolecular cyclization, proposed by Vitaly G. Kiselev and Nina P. Gritsan for isolated FOX-7 molecule,¹⁹ is firstly confirmed in β -FOX-7, as demonstrated in Figure 6. In the thermal decomposition of γ -FOX-7, some fragments like OH and O lead to the break of C=C bond by forming covalent bonds, as illustrated in Figure 7a.

Table 1. Comparison in the highly frequent reactions of the three fox-7 polymorphs heated at 2300 K. P presents the prior reaction products, such as ON, OH, etc. The same as below.

Polymorphs	Time range (ps)	Frequen cy	Reaction
α -FOX-7	1.760-10.396	6	$C_2H_4O_4N_4 \rightarrow C_2H_4O_2N_3 + NO_2$ (R1)
	3.502-14.734	9	$C_2H_4O_4N_4 + P \rightarrow C_2H_3O_4N_4 + H[P]$ (R2)
	7.684	1	$C_2H_4O_4N_4 + P \rightarrow C_2H_4O_3N_4 + O[P]$ (R3)
β -FOX-7	10.496-10.574	2	$C_2H_4O_4N_4 \rightarrow C_2H_4O_2N_3 + NO_2$
	5.548	1	Intramolecular hydrogen transfer (R4)

	2.590-14.042	9	$\text{C}_2\text{H}_4\text{O}_4\text{N}_4 + \text{P} \rightarrow \text{C}_2\text{H}_3\text{O}_4\text{N}_4 + \text{H}[\text{P}]$
	2.714-10.354	3	$\text{C}_2\text{H}_4\text{O}_4\text{N}_4 + \text{P} \rightarrow \text{C}_2\text{H}_4\text{O}_3\text{N}_4 + \text{O}[\text{P}]$
	7.32	1	Intramolecular cyclization (R5)
	0.792-3.672	2	$\text{C}_2\text{H}_4\text{O}_4\text{N}_4 \rightarrow \text{C}_2\text{H}_4\text{O}_2\text{N}_3 + \text{NO}_2$
	1.162-11.928	9	$\text{C}_2\text{H}_4\text{O}_4\text{N}_4 + \text{P} \rightarrow \text{C}_2\text{H}_3\text{O}_4\text{N}_4 + \text{H}[\text{P}]$
⊙-FOX-7	3.720-6.254	3	$\text{C}_2\text{H}_4\text{O}_4\text{N}_4 + \text{P} \rightarrow \text{C}_2\text{H}_4\text{O}_3\text{N}_4 + \text{O}[\text{P}]$
	0.812	1	$\text{C}_2\text{H}_4\text{O}_4\text{N}_4 + \text{O} \rightarrow \text{CO}_4\text{N}_2 + \text{CH}_4\text{ON}_2$ (R6)
	5.146	1	$\text{C}_2\text{H}_4\text{O}_4\text{N}_4 + \text{OH} \rightarrow \text{CO}_4\text{N}_2 + \text{CH}_5\text{ON}_2$ (R7)

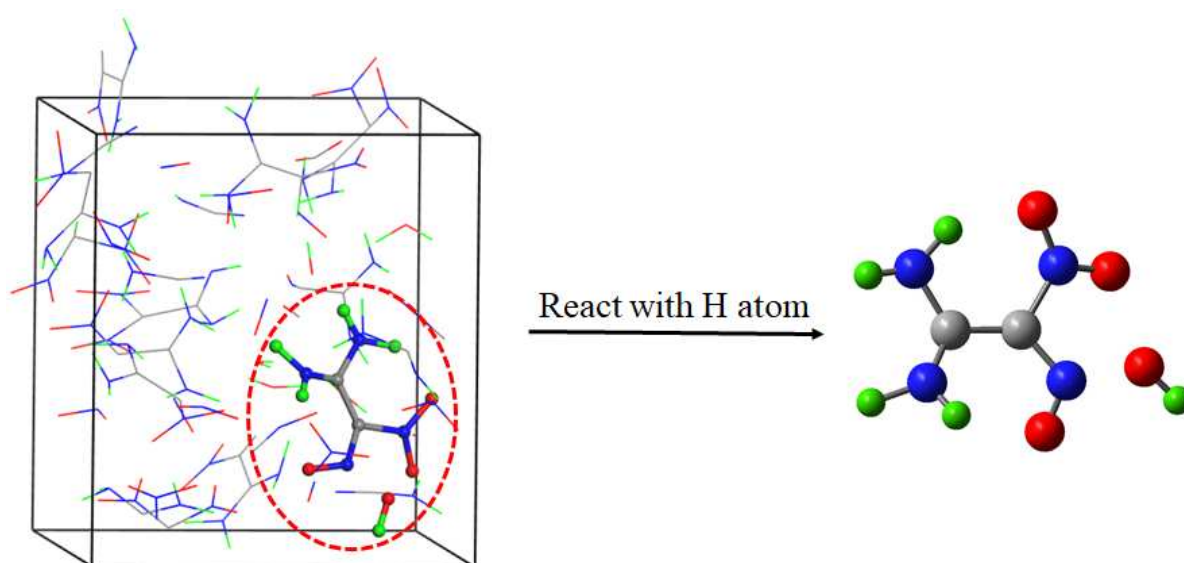


Figure 5. O partition in α -FOX-7 heated at 2300 K.

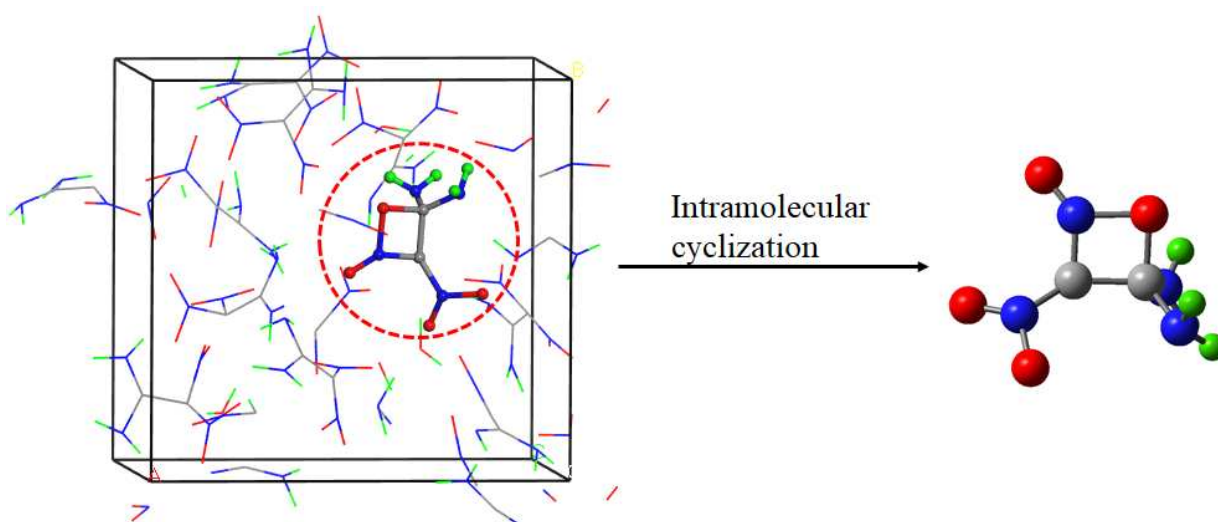


Figure 6. Intramolecular cyclization in heating β -FOX-7 at 2300 K.

The initial reactions and their frequencies during the MD simulation at 3000 K are listed in Table 2. α -FOX-7 is decayed through intra and intermolecular hydrogen transfer, which has been fully discussed in our previous work.¹⁸ Except for the two typical reactions we mentioned above, C=C bond scission occurs in heating γ -FOX-7. Unlike the situation at 2300 K, the rupture of C=C bond takes place without the participation of any other fragment (Figure 7b). It may be caused by the serious molecular deformation, which significantly weakens the strength of the C=C bond.¹⁸

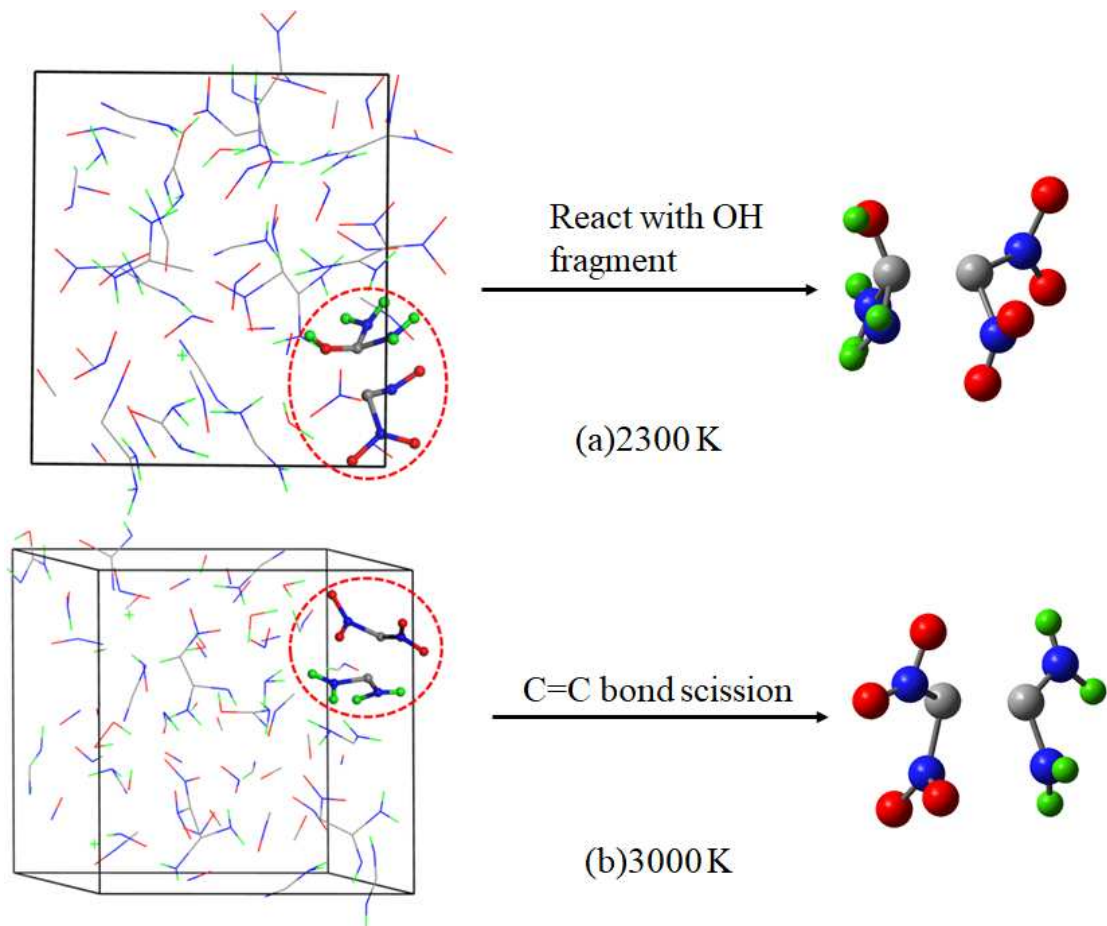


Figure 7. C=C bond scission reaction in heating γ -FOX-7 at 2300 K (a) and 3000 K (b).

Table 2. Comparison in the highly frequent reactions of three FOX-7 polymorphs heated at 3000 K.

Polymorphs	Time range (ps)	Frequency	Reaction
α -FOX-7	0.118-0.540	5	$C_2H_4O_4N_4 \rightarrow C_2H_4O_2N_3 + NO_2$
	0.080	1	Intramolecular hydrogen transfer
	0.078	1	$2C_2H_4O_4N_4 \rightarrow C_2H_3O_4N_4 + C_2H_5O_4N_4$ (R8)
β -FOX-7	0.298-3.810	9	$C_2H_4O_4N_4 + P \rightarrow C_2H_3O_4N_4 + H[P]$
	0.062-0.882	10	$C_2H_4O_4N_4 \rightarrow C_2H_4O_2N_3 + NO_2$
	0.214-1.148	6	$C_2H_4O_4N_4 + P \rightarrow C_2H_3O_4N_4 + H[P]$
γ -FOX-7	0.092-0.562	8	$C_2H_4O_4N_4 \rightarrow C_2H_4O_2N_3 + NO_2$
	0.166-1.462	7	$C_2H_4O_4N_4 + P \rightarrow C_2H_3O_4N_4 + H[P]$
	1.354	1	$C_2H_4O_4N_4 \rightarrow CO_4N_2 + CH_4N_2$ (R9)

The loss of NO₂ and H always occur in the FOX-7 polymorphs heated from 300 to 3000 K, those of H and O atoms take place both in α-FOX-7 and β-FOX-7, and γ-FOX-7 decomposes without the O partition, as listed in Table 3. It shows that the polymorph can influence the initial decomposition step of FOX-7. If the transformation of crystal form is inhibited, the thermal stability of different crystal forms must be considered.

Table 3. Comparison in the highly frequent reactions of three fox-7 polymorphs heated from 300 to 3000 K.

Polymorphs	Time range (ps)	Frequen cy	Reaction
⊙-FOX-7	20.550- 23.028	3	$C_2H_4O_4N_4 \rightarrow C_2H_4O_2N_3 + NO_2$
	22.244- 27.046	11	$C_2H_4O_4N_4 + P \rightarrow C_2H_3O_4N_4 + H[P]$
	24.054- 24.404	2	$C_2H_4O_4N_4 + P \rightarrow C_2H_4O_3N_4 + O[P]$
⊙-FOX-7	21.742- 27.254	7	$C_2H_4O_4N_4 \rightarrow C_2H_4O_2N_3 + NO_2$
	22.872- 26.460	7	$C_2H_4O_4N_4 + P \rightarrow C_2H_3O_4N_4 + H[P]$
	24.694- 25.788	2	$C_2H_4O_4N_4 + P \rightarrow C_2H_4O_3N_4 + O[P]$
⊙-FOX-7	23.704- 26.068	4	$C_2H_4O_4N_4 \rightarrow C_2H_4O_2N_3 + NO_2$
	22.020- 26.358	10	$C_2H_4O_4N_4 + P \rightarrow C_2H_3O_4N_4 + H[P]$
	20.594- 21.900	2	Intramolecular hydrogen transfer

Under the constant temperature heating at 2300 K, the three crystal forms of FOX-7 decompose immediately. As shown in Figure 8a, γ-FOX-7 is the first to decompose, followed by β- and α-FOX-7. Figures 8d and 8e illustrate that the amount of NO and H₂O continues to rise and eventually become major decomposition products in these simulations. Meanwhile, there are plenty of other small molecules formed. In comparison, γ-FOX-7 and β-FOX-7 produce more CO and NH₃ than α-FOX-7, show in Figures 8g and 8h, respectively. Since these two compounds are often regarded as the final products of the thermal decomposition reaction of energetic CHON-containing materials, it can be deduced that the thermal decomposition of β-FOX-7 and γ-FOX-7 proceeds more quickly.

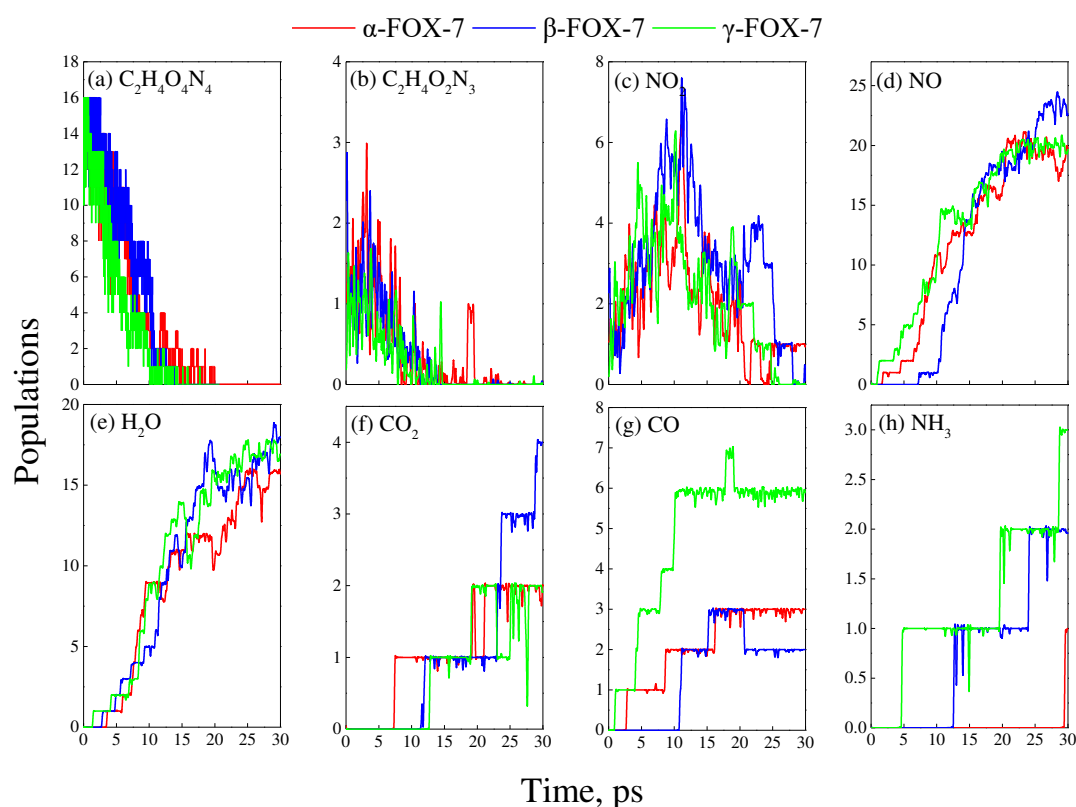


Figure 8. Evolution of some important small molecules, as well as FOX-7, during the thermal decay of the three FOX-7 polymorphs heated at 2300 K.

All the three forms of FOX-7 decompose rapidly at 3000 K. FOX-7 molecules are completely decomposed after 30 ps (Figure 9a). As can be seen in Figure 9b, γ -FOX-7 produces the least O_2 at the initial stage. The NO_2 produced by the decomposition of β -FOX-7 reaches its peak the latest, but the peak is the highest. For the intermediate of NO (Figure 9c), γ -FOX-7 shows the fastest rate of production and the highest consumption. As we can see, γ -FOX-7 produces the fastest and the most N_2O and H_2O (Figure 9f and Figure 9h), consistent with the fastest consumption of intermediate products. For NH_3 (Figure 9g), it is observed that although the output number in γ -FOX-7 was lower than that in α -FOX-7 and β -FOX-7, as it reaches an equilibrium in production firstly.

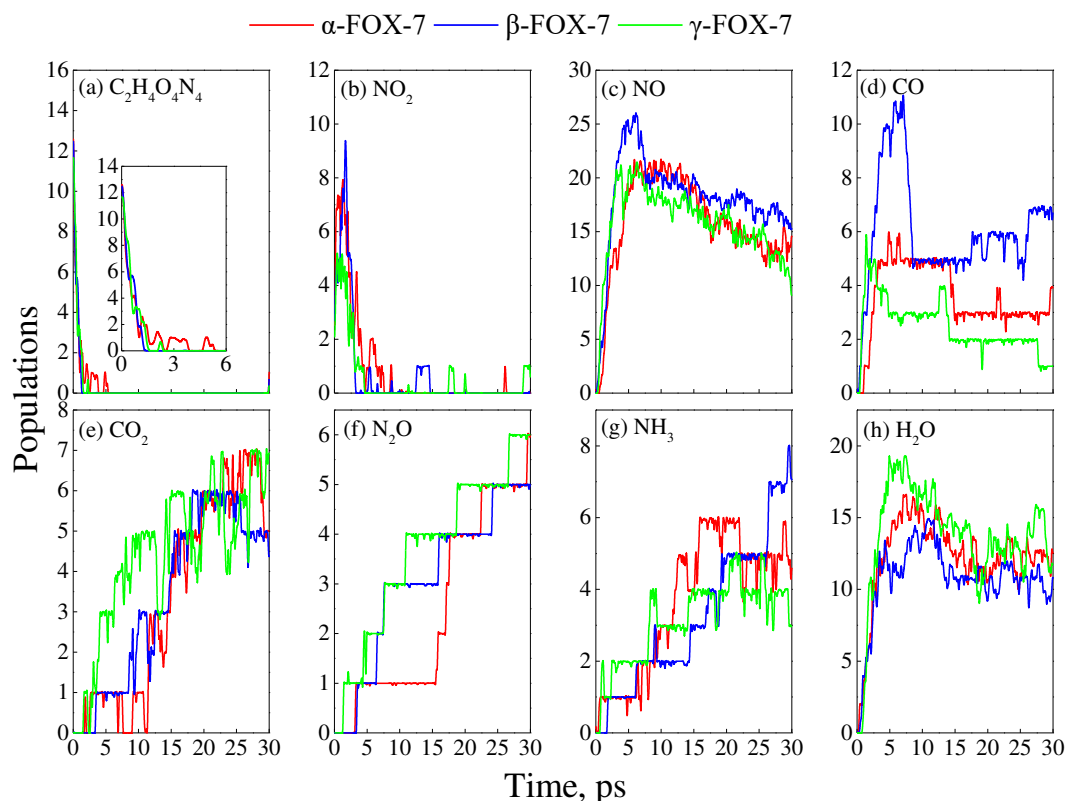


Figure 9. Evolution of some important small molecules, as well as FOX-7, during the thermal decay of the three FOX-7 polymorphs heated at 3000 K.

During the constant-temperature heating, the irreversible decomposition reaction of the three forms of FOX-7 occurs at about 2150 K. As presented in Figure 10a, the decomposition proceeds the fastest at the earlier stage of γ -FOX-7; and when NO_2 is produced (Figure 10b) and reaches the maximum at the same time for γ -FOX-7 and α -FOX-7. This may be attributed the close molecular packing of the both forms. However, a large number of NO_2 is produced while γ -FOX-7 decomposed. A little more NO is produced in β -FOX-7 in contrast to other two polymorphs (Figure 10c). All the three forms of FOX-7 decompose to produce a certain amount of H_2O (Figure 10d). More details of the evolution of some key species are provided in Figures S1-6 of Supporting Information.

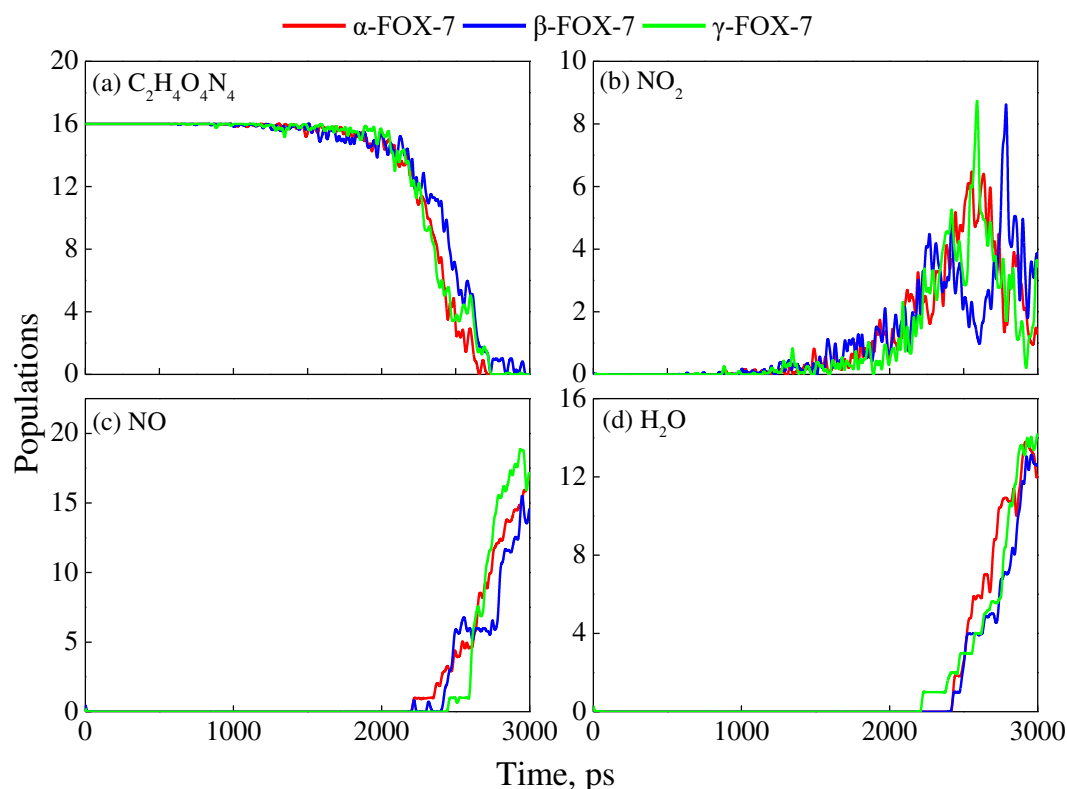


Figure 10. Evolution of some important small molecules, as well as FOX-7, during the thermal decay of the three FOX-7 polymorphs under the programmed heating from 300 to 3000 K.

4. Conclusions

In summary, the SCC-DFTB-MD combined method is employed to reveal the differences of thermal decomposition mechanism of the three forms of FOX-7. We find that in both styles of heating conditions, constant temperature heating and temperature-programmed heating, the polymorphs of FOX-7 have a certain influence on the decomposition mechanism, such as the initial reactions and decomposition rate. It shows the importance of polymorphs in the thermal decomposition, which can hardly be neglected in practice.

Notes: The authors declare no competing financial interest.

Acknowledgment: We greatly appreciate the financial support from the National Natural Science Foundation of China (22173086 and 21875227).

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