Molecular dynamics simulation of initial thermal decomposition mechanism of DNTF

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Research Article

Keywords: Thermal decomposition, Reaction path, Products, Cluster, Molecular dynamics

Posted Date: July 23rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-650084/v1>

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Version of Record: A version of this preprint was published at Journal of Molecular Modeling on April 4th, 2022. See the published version at <https://doi.org/10.1007/s00894-022-05095-x>.

Abstract

In order to understand the thermal decomposition characteristics of 3,4-Bis(3-nitrofurazan-4-yl)furoxan (DNTF), the thermal decomposition reaction of DNTF at 300-4000K temperature programmed and constant temperature of 2000K, 2500K, 3000K, 3500K and 4000K was simulated by ab initio computational molecular dynamics method. The thermal decomposition mechanism of DNTF at different temperatures was analyzed from the aspects of product evolution, cluster, potential energy curve and reaction path. The analysis of products, show that the initial small molecular products are NO, NO₂, CO, CO₂ and N₂, and the final small molecular products are CO₂ and N₂. In the early stage, the ring-opening reaction of furoxan in DNTF structure is the main trigger reaction, and the C-C bond is broken at the initial stage of reaction. The carbon chain structure produced by decomposition forms various cluster structures in the form of C-N bond. In addition, it was found that temperature significantly affects the decomposition rate of DNTF, but does not change its initial decomposition path.

1. Introduction

The detonation process of energetic materials is a complex process involving both physical and chemical interactions, and often occurs in a very short period of time, which make it hard to understand the reaction kinetics in the study of the detonation mechanism of energetic materials. The initial decomposition mechanism of energetic materials at high temperatures is closely related to their detonation phenomena and shock initiation characteristics. Through the study of the thermal decomposition mechanism of energetic materials in the process of detonation, it can help to reveal the energy release law of explosives, and also help to provide theoretical guidance for the study of the thermal stability and sensitivity of explosives.

High energy density materials (HEDM) have become a hot topic of research in the field of energetic materials due to their excellent detonation performance. As a new type of potential HEDMs, furazan compounds have received a lot of attention from scholars at home and abroad because of their high nitrogen content ^[1-3]. 3,4-Bis(3-nitrofurazan-4-yl)furoxan (DNTF) is a hydrogen-free compound containing furazan and furoxan. Because of its high density, low melting point, and better detonation velocity and heat than HMX, it has attracted much attention in the field of energetic materials ^[4-6]. Kotomin et al. ^[7] proved that the detonation performance of DNTF is close to PETN. Ren ^[8] studied the fast thermolysis process of DNTF at different experimental temperatures, and found that the ratio of NO and NO₂ in the gas phase products of DNTF pyrolysis gradually decreased with the increase of temperature. Sinditskii et al. ^[9] considered that the first stage of thermal decomposition of DNTF is the destruction of furoxan ring, and the second stage is the decomposition of nitrofurazan fragments at higher temperature, and its thermal stability is similar to HMX. Li et al. ^[10] studied the thermal decomposition characteristics of DNTF by differential scanning calorimetry(DSC), and found from DSC curve that the thermal decomposition process of DNTF is divided into two stages. In addition, Gao et al. ^[11] compared the thermal decomposition behavior of DNTF at different heating rates, and the results showed that the initial

decomposition temperature of DNTF increased with the increase of heating rate. To sum up, the research mainly explores the thermal decomposition characteristics of DNTF and calculates the relevant kinetic parameters through the experimental means such as rapid temperature transition in-situ pool, temperature jump Fourier transform infrared spectroscopy (T-Jump/FTIR) technology and differential scanning calorimetry, but no relevant research has been done on the initiation reaction, intermediate products and reaction path during the thermal decomposition of DNTF.

With the development of computational science, molecular dynamics and quantum chemistry have become effective methods to analyze the thermal decomposition of energetic materials^[12–14]. The ReaxFF^[15] and ReaxFF-Ig^[16] reaction force field molecular dynamics can simulate the complex chemical reaction changes in large systems over long time scales, and can accurately describe the breaking and formation of chemical bonds, so it is widely used to study the thermal decomposition mechanism of energetic materials such as TNT^[17], CL-20^[18, 19], RDX^[20, 21] and TATB^[22]. Although the ReaxFF reaction force field is optimized by hydrocarbon reaction force field training set, though it has some restrictions for specific molecular structures. In the previous study, after optimizing the unit cell of DNTF by using this force field, it was found that the ring-opening of furoxan ring of DNTF molecule occurred, and the optimized unit cell parameters were quite different from the experimental values. Therefore, it is considered that this force field is not suitable for the simulation of DNTF molecules.

Compared with classical molecular dynamics, *ab initio* Computational Molecular Dynamics (AIMD) equates a polyatomic system to a multi-particle system composed of nuclei and electrons. The density generalized function theory (DFT) approach based on *ab initio* algorithms does not require the provision of force field parameters; it describes the properties of the system in terms of the density distribution function of electrons and solves the Schrödinger equation by the Kohn-Shan equation to obtain the interatomic forces. Due to the higher computational accuracy of DFT compared to *ab initio* calculations based on Hartree-Fock self-consistent-field calculations, it has been successfully applied to study the thermal decomposition of explosives^[23–25].

In this paper, VASP software package^[26] is used for *ab initio* computational molecular dynamics simulation, which is a program for quantum mechanics-dynamics calculation using pseudopotential^[27] and plane wave basis set^[28]. The program adopts the first-principles calculation and iteratively solves Kohn-Shan equation based on density functional theory, which can make the properties of the simulated system closer to reality. Through the analysis of VASP output files, the initial decomposition path, intermediate products, potential energy evolution, the type and quantity of cluster molecules and the evolution trend of species number under different temperature conditions were obtained.

2. Simulation Method

The initial structure of DNTF used in this paper is derived from Cambridge Crystal Database (CCDC)^[29]. The single cell of DNTF was first optimized by Gaussian 09 at the calculated level of M062X/6-311 + G (d, p) to obtain the molecular structure of DNTF at the lowest energy. The bond length and Wiberg bond order

of DNTF were analyzed. By comparing with the standard bond length and Wiberg bond order, we can judge the chemical bond which may be broken during the initial decomposition of DNTF.

The 2×1×1 DNTF cell (176 atoms in total) was optimized by VASP software package at 300 K, as shown in Fig. 1. The optimization process includes two nested processes: electronic iteration and ion relaxation. In the process of electronic iteration, the truncation energy of plane wave base is 240 eV, and the total energy and structural parameters have good convergence. Electronic self-consistent convergence criterion is 1.0×10^{-5} eV. Conjugate gradient method (CG) is used to calculate ion relaxation. The convergence standard of interatomic interaction force is -1.0×10^{-2} eV, the maximum number of steps of ion relaxation is 100 steps.

The lattice parameters under the minimum binding energy and equilibrium structure are obtained, and the optimized atomic position parameters are used as the original parameters of POSCAR file. Molecular dynamics simulation is carried out by using periodic boundary conditions, in which the electron exchange correlation function is in the form of Perdew-Burke-Ernzerh (PBE) in generalized gradient approximation (GGA), and the energy in Brillouin zone is integrated with the point grid accuracy of 1×1×1. The plane wave base truncation energy is 550 eV, and the electron self-consistent convergence criterion is 1.0×10^{-5} eV, and the maximum number of electron self-consistent cycles is 60 steps. The electronic iterative solution adopts residual minimization scheme (RMM) algorithm and uses Nose-Hoove thermostat to control the temperature. The molecular dynamics simulations of DNTF were carried out at 300–4000 K temperature programmed and 2000 K, 2500 K, 3000 K, 3500 K and 4000 K constant temperature for 10 ps. Then the thermal decomposition mechanism of DNTF under aforesaid temperature was analyzed. The choice of the temperature programmed conditions is to accelerate the collision between molecules and the thermal decomposition of DNTF, thus shortening the simulation time. The constant temperature of 2000–4000 K is chosen because the explosive temperature of energetic materials is higher during detonation, and the high temperature environment is more in line with the thermal decomposition conditions of DNTF during detonation.

3. Results And Discussion

3.1 Bond order analyze

The DNTF molecule was optimized by Guassian09 software at the calculated level of M062X/6-311 + G(d, p) as shown in Fig. 2. The corresponding bond length and Wiberg bond order, are shown in Table 1. From Table 1 we can see that the bond order between O2-N11, N16-C22 and N15-C17 are 0.943 Å, 0.903 Å and 0.897 Å respectively, all of which are smaller than the standard single bond order. Therefore, it is tentatively judged that these three bonds are more likely to break during the thermal decomposition of DNTF.

3.2 Feasibility analysis

The 2×1×1 DNTF cell (8 molecules, 176 atoms in total) was optimized by VASP software package, as shown in Fig. 1. The electronic exchange correlation function is in the form of PBE in generalized gradient approximation (GGA), and the energy of Brillouin zone is integrated with the point grid precision of 1×1×1 k points. The plane wave base truncation energy is 240 eV, and the electronic self-consistent convergence criterion is 1.0×10⁻⁵ eV. Table 2 summarizes and compares the bond length of optimized DNTF structure with that of original cell molecules. It can be seen from Table 2 that the maximum error of bond length of DNTF molecule is only 5.50%, which indicates that the structure of DNTF simulated by this method is basically consistent with the experiment. Therefore, it is reasonable to use this pseudopotential to describe DNTF molecule. The optimized structure was analyzed as the initial structure of molecular dynamics simulation. The plane wave base truncation energy is 550 eV, and the step size is controlled to 1 fs, and the same k-point distribution is adopted. The structures were subjected to molecular dynamics simulations for 10 ps at the temperature programmed of 300–4000 K and constant temperatures of 2000 K, 2500 K, 3000 K, 3500 K and 4000 K, respectively, to compare the thermal decomposition mechanism of DNTF at different temperature conditions.

Table 1
Bond length and bond order of DNTF molecule

Coordinate	Bond length/Å	Bond order/ Å	Coordinate	Bond length/Å	Bond order/Å
(1,9)	1.3479	1.114	(10,17)	1.2897	1.643
(1,10)	1.3387	1.136	(11,19)	1.329	1.313
(2,11)	1.3958	0.943	(12,20)	1.2954	1.654
(2,12)	1.3529	1.078	(13,21)	1.2986	1.645
(3,13)	1.3494	1.118	(14,22)	1.2899	1.638
(3,14)	1.3387	1.139	(15,17)	1.4618	0.897
(4,15)	1.2095	1.51	(16,22)	1.4599	0.903
(5,15)	1.1999	1.555	(17,18)	1.4254	1.167
(6,16)	1.2124	1.495	(18,19)	1.4433	1.049
(7,16)	1.1987	1.562	(19,20)	1.4199	1.166
(8,11)	1.2043	1.485	(20,21)	1.4649	1.004
(9,18)	1.3028	1.607	(21,22)	1.423	1.177

Table 2
Bond length of DNTF obtained by experiment and theoretical calculation ^[29]

Coordinate	Reference /Å	simulation value /Å	Error/%	Coordinate	Reference /Å	simulation value /Å	Error/%
(1,9)	1.377	1.400	-1.67	(10,17)	1.288	1.293	-0.39
(1,10)	1.371	1.429	-4.23	(11,19)	1.339	1.375	-2.69
(2,11)	1.440	1.416	1.67	(12,20)	1.306	1.325	-1.45
(2,12)	1.371	1.421	-3.65	(13,21)	1.290	1.361	-5.50
(3,13)	1.380	1.341	2.83	(14,22)	1.296	1.312	-1.23
(3,14)	1.369	1.423	-3.94	(15,17)	1.460	1.400	4.11
(4,15)	1.211	1.240	-2.39	(16,22)	1.455	1.459	-0.27
(5,15)	1.205	1.215	-0.83	(17,18)	1.427	1.406	1.47
(6,16)	1.220	1.181	3.20	(18,19)	1.445	1.413	2.21
(7,16)	1.223	1.238	-1.23	(19,20)	1.416	1.397	1.34
(8,11)	1.199	1.199	0.00	(20,21)	1.472	1.482	-0.68
(9,18)	1.311	1.293	1.37	(21,22)	1.413	1.399	0.99

3.3 Population analysis of thermal decomposition products

3.3.1 Small molecular products

Analysis of the trajectory files shows that the intermediate small molecule products of the thermal decomposition of DNTF include NO, NO₂, N₂O, CO, CO₂ and N₂. Figure 3 demonstrates the evolution curves of DNTF products at different temperatures. Figure 3 demonstrates that the higher the system temperature is, the greater the generation rate of NO and NO₂ is, and the earlier the peak time of evolution curve of NO and NO₂ arrives. As the reaction proceeds, NO₂ and NO show a decreasing trend at different temperature conditions, except for 2000 K. The decay rate of NO₂ and NO molecules decays faster at higher temperatures. It can be inferred that NO and NO₂ appear as intermediate products during the decomposition of DNTF. At 4000K, the content of CO increased significantly compared with other temperature conditions. This is because the increase of temperature will promote the thermal decomposition reaction of DNTF and accelerate the fracture of C-C bond in the DNTF molecule. From the evolution curve of CO at a constant temperature of 4000 K, it can be inferred that CO is also involved in the reaction as an intermediate product.

The initial generation of NO₂ fragments is due to the denitration of DNTF molecules, while the initial decomposition of DNTF has different reaction paths besides denitration. The shed NO₂ fragments will

also react with other small molecules, which limit the amount of NO_2 in the decomposition process under 10, and gradually disappears with the progress of the reaction. However, CO_2 and N_2 still show an upward trend at 10 ps, which suggests that CO_2 and N_2 are the final small molecular products of DNTF decomposition. The evolution of decomposition products of DNTF at constant temperature of 3500 K and 4000 K proves this conjecture. At lower temperature and in the initial stage of reaction, the small molecular products of DNTF thermal decomposition are mainly NO and NO_2 . At higher temperature, the main intermediate products of thermal decomposition of DNTF are NO, NO_2 and CO. Comparing and analyzing the evolution trend of small molecular products of DNTF decomposition under temperature programmed and constant temperature, it can be preliminarily inferred that temperature will affect the thermal decomposition rate of DNTF, but has no significant effect on the evolution trend of its initial thermal decomposition small molecular products.

3.3.2 Cluster structure analysis

Figure 5 Variation curve of number ratio of N, O and C atoms in cluster molecules with time

The N/C and O/C values of the initial structure of DNTF are both 1.33. Figure 5 shows the distribution curve of the ratio of the number of N, O and C atoms in the cluster molecules produced within 10 ps of the thermal decomposition of DNTF. And from the Fig. 5, the N/C and O/C values are less than 1.33 for the four temperature conditions, indicating that a large number of N and O atoms break away from the DNTF molecule at the initial stage of the reaction. This is due to the large amount of small gas molecules such as NO and NO_2 produced at the beginning of the reaction. In addition, the O/C values are smaller than N/C for all four temperature conditions, indicating that the number of O atoms detached from the DNTF structure is greater than the number of N atoms. Figure 6 demonstrates the maximum cluster structure of DNTF within 10 ps under different temperature conditions. It can be seen that there is almost no long chain structure with six carbon atoms in the cluster structure, which indicates that the C-C bond cleavage in the early stage of thermal decomposition of DNTF. After that, the carbon chain structure was recombined with other intermediate products to form a variety of cluster structures in the form of C-N bond.

3.4 Evolution of species number

Potential energy (PE) is the result of the interaction of two molecules, which is related to the strength of the interaction between two molecules, and the interaction between two molecules is related to the relative position of two molecules. Therefore, the evolution of PE can reflect whether the chemical reaction has reached the equilibrium state. It can be seen from Fig. 7 that under the constant temperature conditions of 2500 K, 3000 K, 3500 K and 4000 K, the PE curve suddenly rises and then falls, which indicates that DNTF experienced endothermic process first and then exothermic decomposition. The higher the temperature, the faster the decay rate of PE curve, that is, the greater the initial decomposition rate, and the sooner the system reaches equilibrium. Under the temperature programmed condition of

300–4000 K, with the increase of system temperature, DNTF gradually absorbs energy, and the PE curve peaks at about 6.5ps.

From Fig. 8, it is found that DNTF hardly decomposes at 10 ps at 2000 K, which is consistent with the trend of PE evolution curve. Under the temperature conditions of 2500 K, 3000 K, 3500 K and 4000 K, there is a sudden rise in species number within 2 ps, and the higher the temperature, the greater the slope of the curve and the faster the growth rate of species number. The final number of species is about 42 at 2500 K, about 50 at 3000 K, and about 55 at 4000 K. Therefore, the higher the temperature, the more complex the decomposition pattern of DNTF and the higher the number of species generated. During the temperature programmed process of 300–4000 K, the species number increased rapidly after 5.6 ps, and the final species number was stable at about 45.

3.5 Initial decomposition path analysis

From Table 3, the constant temperature conditions of 2000 K, 2500 K, 3000 K, 3500 K and 4000 K, NO_2 fragments generated by C- NO_2 bond cleavage in DNTF structure almost occur within 1.5 ps. Especially at 2000 K, 2500 K and 3000 K, the denitration frequency of DNTF reached the maximum. At 3500 K and 4000 K, high temperature accelerates the cleavage of C-C bond in DNTF, thus reduce the frequency of $\text{C}_6\text{O}_8\text{N}_8 = > \text{C}_6\text{O}_6\text{N}_7 + \text{NO}_2$ reaction. It can be seen from the decomposition reaction equation of DNTF under the temperature programmed condition of 300–4000 K that a large amount of NO_2 and NO are generated in the initial stage of thermal decomposition of DNTF, which significantly increases the amount of NO_2 and NO in the system. This phenomenon is consistent with the evolution trend of NO_2 and NO in Fig. 3, and so is that with the thermal decomposition path of DNTF under constant temperature, indicating that the initial thermal decomposition path of DNTF under the temperature programmed is consistent with that under constant temperature.

In addition to direct NO_2 removal, DNTF molecules are accompanied by NO removal and carbon chain cleavage, which leads to the increase of reaction types and the decrease of frequency. This is one of the reasons why the frequency of all the reactions in Table 3 is not high. At 2000 K, a relative lower temperature, the initial decomposition of DNTF is mainly denitration, and the small molecular product produced is mainly NO_2 , as shown in Fig. 3. Under the constant temperature conditions of 2500 K, 3000 K, 3500 K and 4000 K, the production amount and production rate of small molecular product NO will increase significantly, which indicates that the increase of temperature will significantly promote the reaction of NO production.

Table 3
Reaction path of DNTF within 10 ps

T(K)	Reaction time/ps	Frequencies	Primary reactions
300-4000K	4.0-5.9	2	$C_6O_8N_8 \rightarrow C_5O_6N_6 + CO_2N_2$
	5.6-6.8	2	$C_6O_8N_8 \rightarrow C_6O_6N_7 + NO_2$
	4.0-5.7	1	$C_6O_8N_8 \rightarrow C_2O_3N_3 + C_4O_5N_5$
	5.3-5.3	1	$C_6O_8N_8 \rightarrow C_6O_4N_6 + NO_2 + NO_2$
	5.7-5.7	1	$C_6O_8N_8 \rightarrow C_6O_7N_7 + NO$
	5.9-5.9	1	$C_6O_8N_8 \rightarrow C_5O_4N_5 + CO_2N_2 + NO_2$
2000K	0.3-8.9	4	$C_6O_8N_8 \rightarrow C_6O_6N_7 + NO_2$
	0.9-7.3	2	$C_6O_8N_8 \rightarrow C_5O_6N_6 + CO_2N_2$
	6.5-8.9	2	$C_6O_6N_7 + C_6O_6N_7 \rightarrow C_{12}O_{12}N_{14}$
	9.2-9.2	1	$C_6O_6N_6 \rightarrow C_6O_5N_5 + NO$
	2.7-2.7	1	$C_6O_8N_8 \rightarrow C_5O_3N_5 + CO_3N_2 + NO_2$
2500K	0.1-1.5	4	$C_6O_8N_8 \rightarrow C_6O_6N_7 + NO_2$
	0.1-2.2	2	$C_6O_8N_8 \rightarrow C_2O_3N_3 + C_4O_5N_5$
	1.3-5.7	2	$C_3O_4O_4 \rightarrow C_3O_2N_3 + NO_2$
	2.1-4.2	2	$NO_2 \rightarrow O + NO$
	6.9-9.6	2	$CN + NO \rightarrow CON_2$
	9.4-9.4	1	$C_2O_3N_3 + CO \rightarrow C_2O_2N_3 + CO_2$
3000K	0.1-0.2	4	$C_6O_8N_8 \rightarrow C_6O_6N_7 + NO_2$
	2.1-9.7	3	$CO_2N \rightarrow CO + NO$
	8.8-8.8	2	$C_3O_2N_3 \rightarrow C_2ON_2 + CON$
	0.5-0.5	2	$C_6O_6N_7 \rightarrow C_6O_5N_6 + NO$

From the previous analysis, it is known that the C-NO₂ bond in DNTF molecule is easy to cleavage, and the O2-N11 bond in its furoxan ring is also a weak chemical bond. However, the reaction equations in Table 3 cannot explain this phenomenon. Therefore, it is necessary to analyze the trajectory file of DNTF reaction deeply.

T(K)	Reaction time/ps	Frequencies	Primary reactions
	0.5–0.5	1	$C_6O_7N_7 \rightarrow C_6O_4N_5 + NO_2 + NO$
	0.7–0.7	1	$C_6O_8N_8 \rightarrow C_6O_5N_6 + NO_2 + NO$
3500K	0.3–0.3	1	$C_6O_8N_8 \rightarrow C_6O_7N_7 + NO$
	0.4–1.5	4	$NO_2 \rightarrow O + NO$
	2.8–8.7	4	$C_2O_3N \rightarrow CO_2 + CON$
	0.1–0.1	3	$C_6O_8N_8 \rightarrow C_6O_6N_7 + NO_2$
	1.7–9.0	2	$CON_2 \rightarrow CN + NO$
	0.6–7.6	2	$NO + NO \rightarrow N_2O_2$
	5.6–8.8	2	$CON + NO \rightarrow CO + N_2O$
	2.9–9.7	2	$C_3O_2N_4 \rightarrow C_3ON_3 + NO$
4000K	0.3–2.9	4	$O + NO \rightarrow NO_2$
	1.6–9.8	4	$C_2O_3N \rightarrow CO_2 + CON$
	0.7–5.9	3	$N_2O_2 \rightarrow NO + NO$
	1.6–2.9	2	$CO_2N + NO \rightarrow CO + N_2O_2$
	2.1–2.6	2	$C_2ON_4 + NO \rightarrow C_2O_2N_3 + N_2$
	6.7–8.9	2	$C_2O_2N + N_2O \rightarrow C_2O_3N + N_2$
	0.1–0.1	2	$C_6O_8N_8 \rightarrow C_6O_6N_7 + NO_2$
<p>From the previous analysis, it is known that the C-NO₂ bond in DNTF molecule is easy to cleavage, and the O2-N11 bond in its furoxan ring is also a weak chemical bond. However, the reaction equations in Table 3 cannot explain this phenomenon. Therefore, it is necessary to analyze the trajectory file of DNTF reaction deeply.</p>			

The 0-0.5 ps trajectory file was split into 100 frames and analyze the frequency of ring-opening between furoxan and furazan and nitro detachment in turn, as shown in Fig. 10. Figure 9 shows the case of DNTF furazan ring-opening and furoxan ring-opening. It can be seen from Fig. 10 that the ring-opening reaction frequency of furoxan is extremely significant under other temperature conditions except 4000 K, and all of them are before DNTF denitration reaction. For example, at 3000 K, the first ring-opening reaction of furoxan appeared in the third frame (0.015 ps) of DNTF. Therefore, the ring-opening reaction of furoxan is the main trigger reaction of its thermal decomposition. Of course, we can also find that within 0.5 ps, these reactions are to some extent reversible, and the lower the temperature the smaller the

decomposition degree of DNTF molecules, which is obvious under the constant temperature condition of 2000 K and the temperature programmed process of 300–4000 K. With the increase of temperature, for example, at 4000 K, the C-C bond of DNTF molecule cleavage a lot, which leads to the decrease of the ring-opening reaction frequency of DNTF, so only the reaction frequency within 9 frames is counted. In addition, the ring-opening of DNTF molecule furoxan precedes the ring-opening of furazan and the denitration during the temperature programmed reaction, which is consistent with the decomposition mechanism of DNTF at constant temperature. To sum up, the thermal decomposition of DNTF firstly occurs the ring-opening reaction of furoxan, then the ring-opening reaction of furazan and denitration reaction, and finally the thermal decomposition reaction of molecular fragments, which is consistent with the research results of Sinditskii [9].

4. Conclusion

The reaction process of DNTF thermal decomposition at 300–4000 K temperature programmed and constant temperature 2000 K, 2500 K, 3000 K, 3500 K and 4000 K was analyzed, and the initial reaction path of DNTF thermal decomposition was obtained. It is found that the ring-opening reaction of furoxan occurs first in the thermal decomposition of DNTF. Then, furazan ring-opening and the C-NO₂ bond cleavage of DNTF molecule, and furoxan ring-opening was the main trigger reaction at the initial stage of the reaction. By comparing the evolution trend of species number of DNTF under six temperature conditions, it can be seen that the higher the temperature, the faster the decomposition rate of DNTF and the more species generated.

The initial stage of the thermal decomposition reaction of DNTF involves the C-C bond cleavage, and the carbon chain structure resulting from the cleavage combines with other intermediate products in the form of C-N bonds to form a variety of cluster structures. At lower temperature and in the initial stage of thermal decomposition reaction, the small molecular products are mainly NO and NO₂, while the thermal decomposition intermediate products at high temperature are mainly NO, NO₂ and CO. With the progress of the reaction, these small molecules will react with some short chain structures to form the final products N₂ and CO₂.

By comparing and analyzing the evolution trend of small molecule products, reaction path and trigger reaction of DNTF thermal decomposition at 300–4000 K temperature programmed and different constant temperatures, it is found that temperature affects the initial thermal decomposition rate of DNTF, but does not change the initial thermal decomposition mechanism of DNTF.

Declarations

Funding: No funding was received to assist with the preparation of this manuscript.

Conflicts of interest/Competing interests: The authors have no conflicts of interest to declare that are relevant to the content of this article.

Availability of data and material: All data generated or analyzed during this study are included in this published article.

Code availability: N/A

Authors' contributions: Hui Bai and Yiming Luo conceived and designed the study. Hui Bai, Jiang Jun and Wenjun Hu performed simulation calculations. Hui Bai wrote the paper. Ruijun Gou and Shuhai Zhang reviewed and edited the manuscript. All authors read and approved the manuscript.

Ethics approval: N/A

Consent to participate: N/A

Consent for publication: N/A

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Figures

Figure 1

Unit cell structure of DNTF

Figure 2

Molecular structure of DNTF

Figure 3

Product evolution curve of DNTF in 10 ps at different temperatures

Figure 4

The change curve of cluster number during DNTF thermal decomposition

Figure 5

Variation curve of number ratio of N, O and C atoms in cluster molecules with time

Figure 6

Structure of the largest cluster molecule at different temperatures

Figure 7

Evolution of potential energy with time at different temperatures

Figure 8

Species number evolution curve of DNTF within 10ps

Figure 9

Schematic diagram of DNTF furazan ring-opening and furoxan ring-opening

Figure 10

Frequency curve of ring-opening reaction of DNTF at various temperatures