

Theoretical insights into the synthesis mechanism of two amino-substituted derivatives of FOX-7

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September 13, 2022

Abstract

FOX-7 is a typical high-energy and low-sensitivity material. Due to the unique “push-pull” nitroenamine structure, abundant derivatives with good performance can be synthesized. DFT method is used to study the synthesis mechanism for two FOX-7 amino-substituted derivatives. The synthesis mechanism of amino-substituted derivative MTNzA is cyclization followed by isomerization, which is different from the pathway of isomerization followed by cyclization proposed by previous authors. Carbohydrazide is tend reacted with two FOX-7 to produce BADCh, rather than ring formation with one FOX-7.

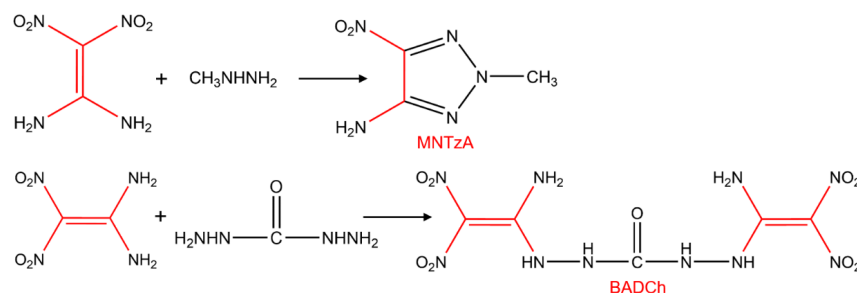
Introduction

Energetic materials are widely used in the military and aerospace fields as explosives or propellants [1]. The future research and development direction of energetic materials is mainly to synthesize more suitable high-energy, low-sensitivity new energetic materials. In 1998, 1,1-diamino-2,2-dinitroethylene (FOX-7) was first synthesized by Latypov et al. [2]. Its energy is close to the typical high-energy materials RDX and HMX [3] that have been put into production now. Its sensitivity is low, and close to the typical low-sensitivity energetic materials TATB [4]. Therefore, studying the characteristics of FOX-7 is of great significance for the search for high-energy and low-sensitivity energetic materials. There is a highly polarized carbon-carbon double bond in the middle of the FOX-7 molecule, and the carbon-carbon double bond is flanked by two amino groups and two nitro groups. This nitroenamine structure has a unique electronic “push-pull” property. Due to the electron-pushing effect of the amino group and the electron-pulling effect of the nitro group, a stable carbon-carbon double bond structure is formed, and various isomers and resonance structures can also be formed through electron rearrangement [5-7]. The positively charged end of the carbon-carbon double bond can be attacked by the nucleophile, resulting an addition reaction is carried out. Since the amino group is an electron-pushing group and is positively charged, the substitution reaction of the amino group can be reacted with nucleophile. In addition, the nitrogen atom of the amino group is sp^3 hybridized and has a lone pair of electrons, which can also react with electrophilic reagents. [8,9]. Based on this “push-pull” electronic structure, there are many reactive sites on the molecular structure of FOX-7, so a variety of potential new energetic materials can be synthesized.

The nucleophilic substitution reaction of single amino group is an important reaction type based on FOX-7. In the reaction of FOX-7 with methylamine, an amino group on FOX-7 is substituted by methylamine to generate 1-amino-1-methylamino-2,2-dinitroethylene (AMFOX-7) [10], In the above reaction, the ring formation reaction based on both amino groups are substituted is difficult to proceed, and it may be caused by the steric hindrance effect according previous reports [11,12]. The reaction that two amino groups are substi-

tuted into a ring is also an important reaction type based on the FOX-7 reaction. In the reaction of FOX-7 with ethylenediamine, both amino groups on FOX-7 is substituted, resulting in a cyclic 2-dinitromethylene-1,3-diazacyclopentane (DNDZ) product at the original position of the two amino groups. There is no single amino-substituted product in the above reaction, which may be due to the strong stability and lower energy of the cyclic compound. In addition, due to the existence of lone pair electrons on both amino groups of FOX-7, such a structure itself can also react as a nucleophile, and the cyclic compound 4,5-dihydroxy-2-(dinitromethylene)-imidazolidine (DDNI) [13] can be generated from the reaction of FOX-7 with glyoxal based on this. In addition, other types of reactions can occur with FOX-7 [14-17].

The polyazole ring has great potential as the molecular framework of energetic materials [18], and Click reaction is still the main synthetic method for synthesizing 1,2,3-triazole rings [19]. New energetic material molecules based on molecular framework of polyazole ring can be constructed by substitution reaction of amino group on FOX-7. If the mechanism of substitution of amino groups into ring can be clarified, a new method for the synthesis of polyazole rings may be developed based FOX-7. In scheme 1, an important synthetic work on amino substitution is reported by Xu et al. [20], including: FOX-7 and methylhydrazine (CH_3NHNH_2) is cyclized to form 2-methyl-5-nitro-1,2,3-triazol-4-amine (MNTzA), and 1,5-bis(1-amino-2,2-dinitrovinyl) (BADCh) is formed by mono-amino substitution of two FOX-7 and carbonylhydrazide (CHZ). The possible synthesis mechanism of MNTzA is also proposed by Xu, but through our verification, a more suitable reaction mechanism is found. Moreover, the mechanism of mono-amino substitution and ring formation in the reaction between FOX-7 and CHZ is also compared.



Scheme 1. reaction steps for the synthesis of MNTzA and BADCh by FOX-7

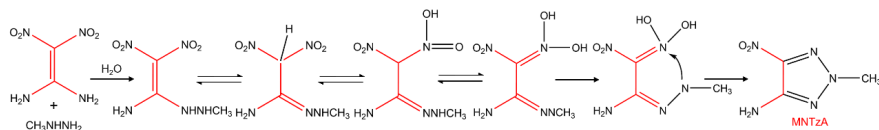
Computational details

All geometric optimizations are performed at the density functional theory (DFT) level by using hybrid B3LYP functionals [21-23] with the basis set def2-TZVP [24,25]. The properties of the optimized stationary points are characterized by the frequency calculations at the same theoretical level, with no imaginary frequency for all reactant, intermediate, and product configurations, and an imaginary frequency mode for all transition states (TSs). Thermal correction of the electron energy for the optimized geometry was estimated at an experimental temperature of 373 K and 1 atmosphere, based on frequency calculations. Water was used as the solvent, and PCM method [26] was used for SCRF calculation to simulate the solvent effect. The intrinsic reaction coordinates (IRC) [27] calculations from first-order saddle points were performed to locate the local minimum of the reaction path, which is represented by a solid line in the energy distribution. In order to obtain more accurate electron energies and reaction barrier heights, single-point calculations based on the optimized geometry is further performed by using the B3LYP functional with a larger basis set def2-QZVP [28]. Gaussian 16 program [29] is used for all DFT calculations.

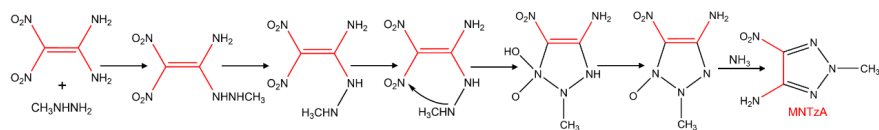
3. Results and discussions

In Scheme 2, the amino group on FOX-7 is substituted by CH_3NHNH_2 , and the H on the $-\text{NHNHCH}_3$ group is transferred to the C attached to the nitro group. Subsequent multi-step isomerization reactions are carried out, and finally a ring formation reaction is carried out, and a triazole ring structure is formed. In Scheme

3, a new reaction path is proposed, and the lower energy barrier of this path is also proved by theoretical calculations. The biggest difference between Scheme 3 and Scheme 2 is that after the substitution reaction between CH_3NHNH_2 and FOX-7, the triazole ring is formed through the formation of a bond between the N on the $-\text{NHNHCH}_3$ group and then the N on the nitro group, then isomerization reactions are carried out.



Scheme 2, the reaction pathway to generate MNTzA proposed by Xu.



Scheme 3, the reaction pathway to generate MNTzA in this paper.

3.1 The reaction pathway of MNTzA

In Figure 1, the C on the alkenyl group of FOX-7 is gradually approached by the N on the amino group of CH_3NHNH_2 , and the N atom on the amino group of FOX-7 is gradually approached by the H atom on the amino group, resulting in a synergistic reaction and generating intermediate IM1. The NH_3 connected to IM1 is very unstable and breakage of C-N bond is carried out immediately, generating a stable intermediate IM2 with relatively low energy.

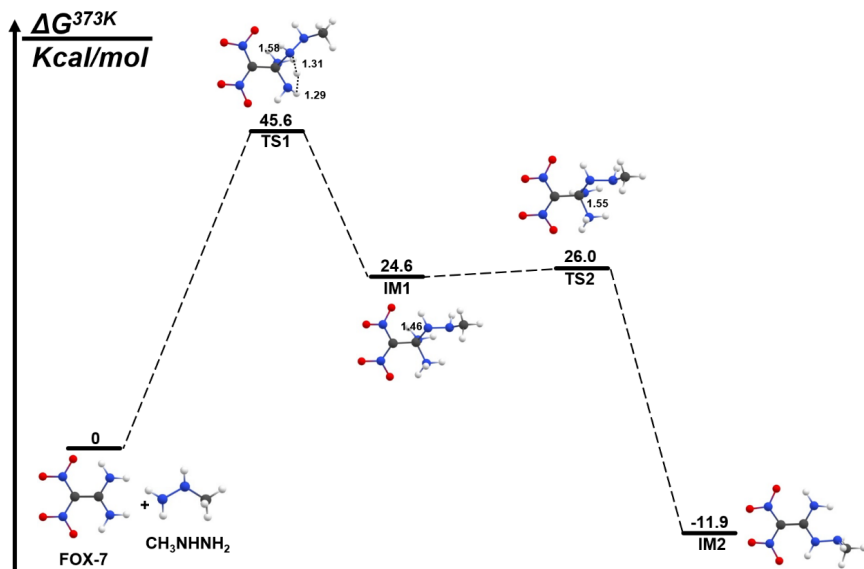


Figure 1. Gibbs free-energy profile for the substitution reaction of the amino group of FOX-7 by CH_3NHNH_2

In Figure 2, the subsequent reaction of the intermediate IM2 is carried out according to the reaction path proposed by Xu [20]. The H on the $-\text{NHNHCH}_3$ group of IM2 is transferred to another C on the alkenyl group, via the transition state TS3 with an energy barrier of 44.3 kcal/mol, forming the intermediate IM3.

Subsequently, the H on the C of the alkenyl group of the intermediate IM3 is transferred to the O of the nitro group to form the intermediate IM4, in which the energy barrier of the transition state TS4 is higher, and this step is difficult to carry out. The H on the N of the -NNHCH₃ group of IM4 is approached to the O on the nitro group through the rotation of the dihedral angle to form IM5, which is conducive to the next H transfer reaction. The H on the N of the -NNHCH₃ group of IM5 is transferred to the O on the nitro group, forming the intermediate IM6 with two H atoms in the nitro group. Subsequently, the N atom on the nitro group is approached by the N atom on -NNCH₃ group, forming IM7 with a triazole ring structure. IM7 is unstable, and the -OH group on the N of the triazole ring is immediately combined by H to decompose into a H₂O molecule and stable IM8 intermediates. The NH₃ generated earlier in this reaction is combined with IM8 to form the product MNTzA. According to the reaction energy barrier, it can be seen that the TS4 is higher in the reaction path of the transfer of H on the alkenyl group of IM3 to O on the nitro group, so the reaction path proposed by Xu is carried out difficultly.

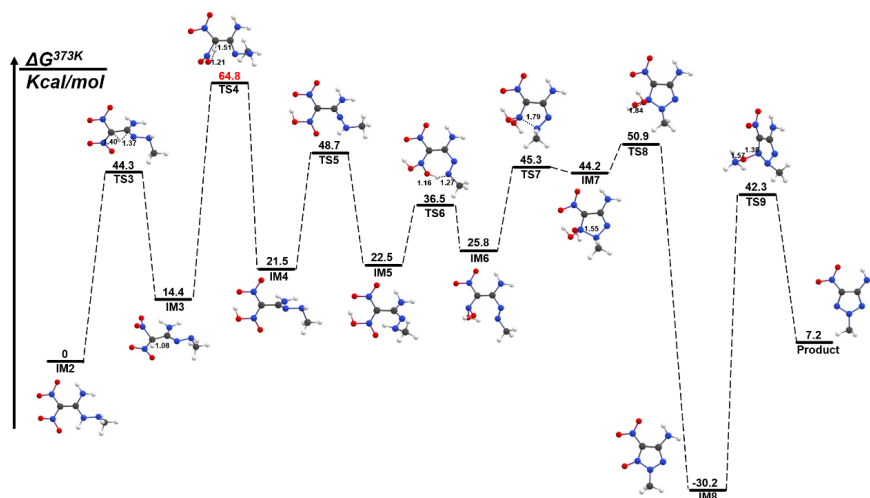


Figure 2. Gibbs free-energy profile for the production of MNTzA according scheme 2.

In Figure 3, the cyclization reaction of the triazole ring is performed first. Through the rotation of the dihedral angle, the N on the -NHNHCH₃ group is approached to the N on the nitro group, forming an intermediate IM3', which facilitates the subsequent formation of a triazole ring structure. The triazole ring is formed by the formation of a bond between the N on the -NHNHCH₃ group of IM3' and the N on the nitro group, and the H on the -NHNHCH₃ group is transferred synergistically to the O on the nitro group, forming intermediate IM4'. The H on the triazole ring of IM4' is transferred to the -OH group to generate the H₂O molecule and the intermediate IM8. Finally, the NH₃ generated earlier in this reaction is combined with IM8 to form the product MNTzA. Comparing the reaction mechanisms of Figure 2 and Figure 3, it can be found that the energy barrier of the rate-determining step TS4' is lower than that of TS4, and the reaction pathway of Figure 2 is more likely to proceed.

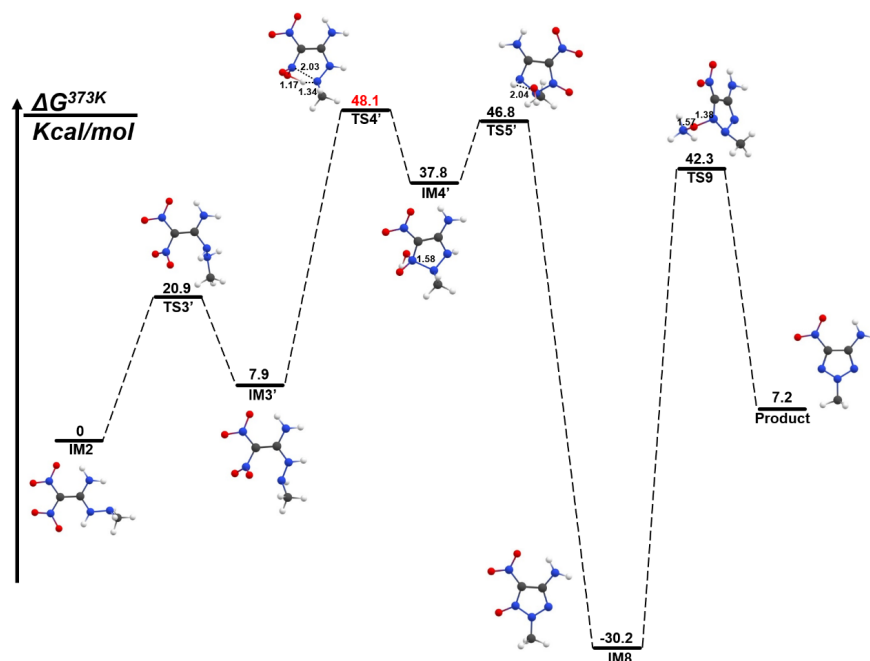


Figure 3. Gibbs free-energy profile for the production of MNTzA according scheme 3.

3.2 The reaction pathway of BADCh

In Figure 4, the amino group of FOX-7 is first substituted with CHZ. When the N on the amino group of CHZ is combined with the C on the alkenyl group of FOX-7, the H is also transferred to the N on the alkenyl group, resulting in the intermediate IM10. IM10 is unstable and the C-N bond is broken, generating NH₃ molecules and a stable intermediate IM11.

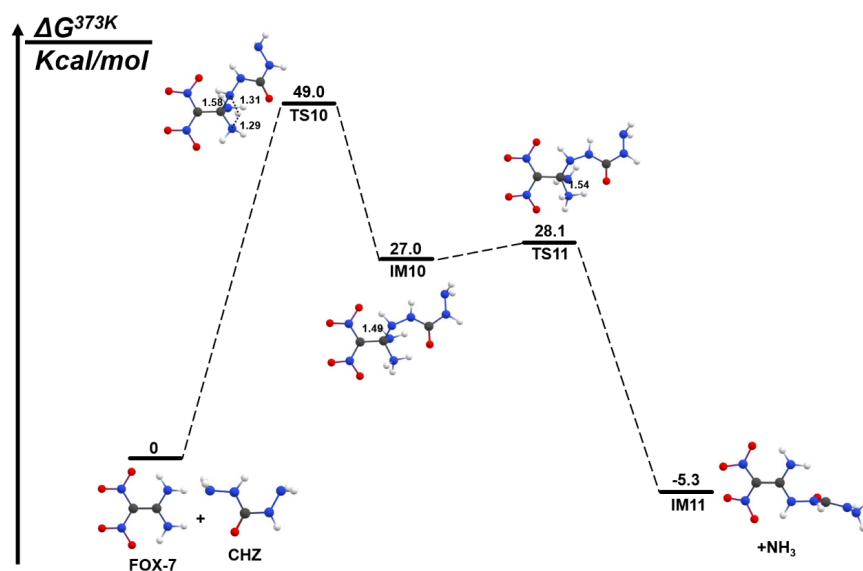


Figure 4. Gibbs free-energy profile for the substitution reaction between FOX-7 and CHZ

Due to the presence of amino groups at both ends of CHZ, substitution reaction is also carried out between IM11 and the second FOX-7. In Figure 5, the amino group on the second FOX-7 is substituted by the amino group on the -NHNHC=ONHNH₂ group of IM11, forming IM12. IM12 is unstable, and the bond breaking process is performed quickly, generating the NH₃ molecule and the final product BADCh. Since CHZ has amino groups on both sides and there are two sites that can be substituted with FOX-7, CHZ can also easily react with two FOX-7 molecules, respectively.

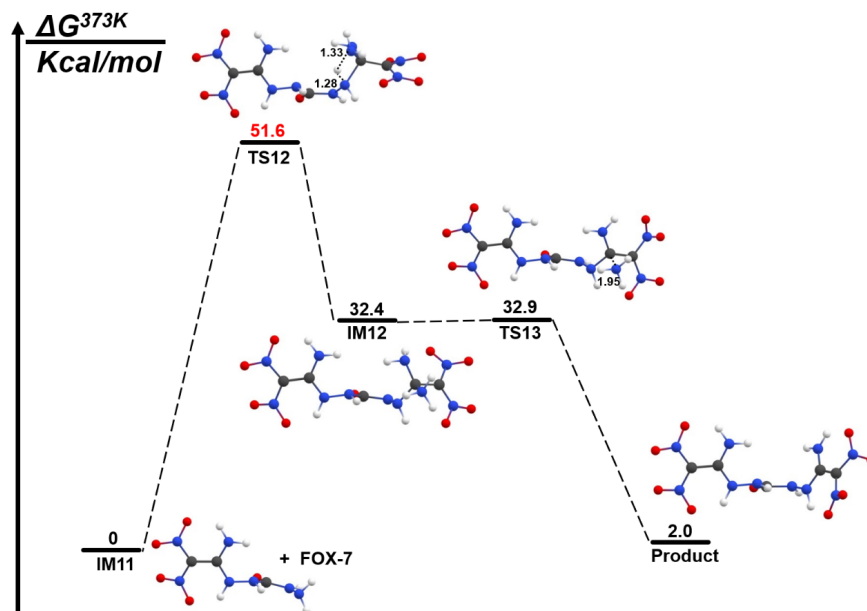
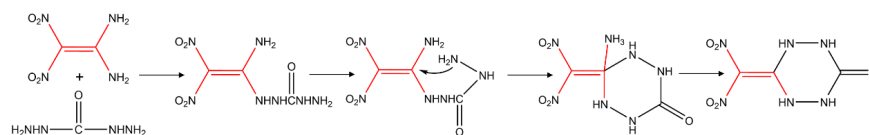


Figure 5. Gibbs free-energy profile for the substitution reaction between the second FOX-7 and CHZ

There are two reactive sites on the FOX-7 molecule that can be substituted by CHZ. Therefore, it is necessary to verify why the pathway of bisamino substitution into the ring is difficult to proceed. In Scheme 4, after an amino group on FOX-7 is substituted by CHZ, another amino group is also substituted by CHZ, and finally a six-membered ring structure is formed.



Scheme 4, the reaction pathway of FOX-7 with carbohydrazide to form a ring

In figure 6, the other amino group on the IM11 molecule continues to be substituted by the -NHNHC=ONHNH₂ group and does not react with the second FOX-7. The formation of IM12' is through the rotation of the dihedral angle of -NHNHC=ONHNH₂ group on IM11, and the subsequent C-N bond binding and ring formation reaction are facilitated by the rotation of the dihedral angle to the appropriate position. The N on the amino group of the -NHNHC=ONHNH₂ group of IM12' is bonded with C on the alkenyl group to form a six-membered ring structure and H transfer process is proceeded synchronously, resulting in formation of IM13'. Since IM13' is unstable, IM13' is decomposed into NH₃ and the cyclic product IM14'. It can be seen that the energy barrier of TS13' is higher than that of TS12, and the two amino reaction sites of CHZ are tend to react with two FOX-7s respectively, but not easily to form a ring reaction with the two amino groups of one FOX-7.

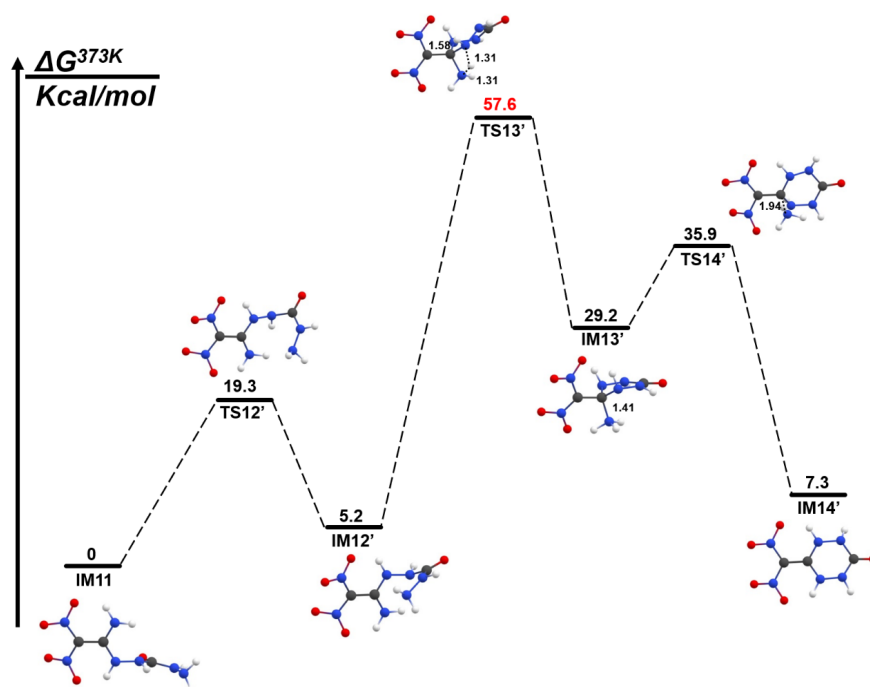


Figure 6. Gibbs free-energy profile for the substitution reaction of the second amino group on one FOX-7

4. Conclusion

In the reaction of FOX-7 and CH_3NHNH_2 , the reaction mechanism is more inclined to form a stable triazole ring structure first, and then molecular isomerization is proceeded, generating the corresponding product finally. In the reaction of FOX-7 and CHZ, there are two sites on CHZ that can react with the amino group of FOX-7. the two reaction sites of CHZ are tend to react with two FOX-7s respectively, rather than a bisamino substituted ring formation reaction with one FOX-7 molecule.

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