# Theoretical study on the thermal dissociation of FOX-7 promoted by NO2

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# ABSTRACT

1,1-diamino-2,2-dinitroethene (FOX-7) is a novel energetic material with high performance and low sensitivity. In order to deeply understand the reaction mechanism in the initiation “hot spots” of FOX-7 and reveal the growth mechanism of these initiation "hot spots" in the explosion process, the detailed mechanisms of bimolecular reaction of NO2 and FOX-7, as well as the subsequent reactions have been investigated by the quantum chemical calculations. The mechanism of NO2 and FOX-7 bimolecular reaction and the catalytic effect of NO2 were revealed by three key dissociation paths. It is demonstrated that the NO2 molecule plays an important role in promoting the decomposition of the FOX-7 molecule, and the main exothermic pathways were the reactions between oxidizing intermediates (NO, NO2), and reducing intermediates (CO, NH3).

# INTRODUCTION

The study on the mechanism of the initiation reaction process of energetic materials can help people deeply understand the essence of the explosion reaction of energetic materials. It is also very important to reveal the relationship between the sensitivity of energetic materials and their microstructure. In order to deeply understand the reaction mechanism of the initiation reaction process of energetic materials, a large number of experimental and theoretical studies have been carried out. Quantum chemical calculation is a very important research method. The reaction mechanism of a large number of important energetic materials has been studied in detail by quantum chemical calculations.

“Hot spot” theory is a widely accepted detonation theory of energetic materials. In this theory, the explosion of energetic materials starts from the “hot spots” under the stimulation by impact or shock waves. In this initiation "hot spot", energetic material molecules are in a very dense environment. In this state, in addition to the unimolecular reaction process of energetic material molecules, there are also a large number of bimolecular reactions, including the reaction between energetic material molecules, the reaction between molecular fragments produced by decomposition, and the reaction between active reaction intermediates and unreacted molecules. Because the chemical reactions in the “hot spots” are so complex, most quantum chemical calculation research is still mainly focused on the isomerization and decomposition of a single molecule, and the in-depth study of these bimolecular reactions is far from enough.

1,1-diamino-2,2-dinitroethene (FOX-7) is a novel energetic material with high performance and low sensitivity1-2 and is expected to replace sensitivity energetic materials, such as RDX (cyclo-1,3,5-trimethylene-2,4,6-trinitramine)3. The FOX-7 has been extensively studied since its first successful synthesis in 1998 for its excellent performance4. Both computational and experimental methods have been used to study the dissociation pathway of FOX-75-10.

In 2014, Liu and co-workers11 found that the main initial dissociation path of the FOX-7 is C-NO2 bond cleavage by using different theoretical methods, and the concentration of the formed NO2 increases first and then decreases. Meanwhile, they proposed that the main products are HCN, NO, NH3 and H2O. Zhao *et al.*12 calculated the products of FOX-7 dissociation and concluded that N2,H2O, CO2, N2O are the main products and NH3 is the minor product.The result also proved that NO2 is an important intermediate product, whose variation tendency of concentration is consistent with the previous research11. The investigation of Burnham *et al.*13also showed the same trend of NO2 concentration with FTIR.

Although massive studies have focused on the dissociation of FOX-7, two important problems need to be solved：（1）Most of studies only took account of the major pathways of the dissociation of FOX-7 single molecule. Based on previous theoretical and experimental results on NO2 concentration variation in the dissociation process of FOX-7, for such a high molecular density in the initiation "hot spot", NO2 molecules with very high reactivity will inevitably react with other molecules. Although bimolecular reactions have been explored in the previous literature14, the mechanism of the reaction process between NO2 and FOX-7 molecules is still far from perfect and needs more comprehensive and in-depth discussion.（2）In the initiation process, the "hot spot" needs to develop continuously until detonation occurs, which requires the reaction in the hot spot to continuously generate enough heat to ensure the maintenance and growth of the "hot spot". However, from the main reaction paths reported in the existing literature, the main exothermic reaction in the initial stage of initiation was not clear.

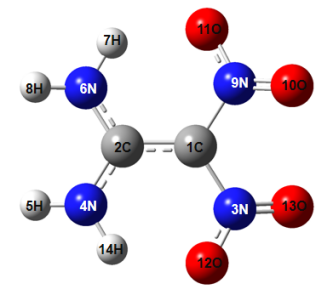
In order to solve the above two problems, we used quantum chemical calculations to deeply study various chemical reactions between NO2 molecule and FOX-7 molecule, as well as the detailed reaction process of subsequent intermediates. It is revealed that the NO2 molecule plays an important role in promoting the decomposition of the FOX-7 molecule, and it is clear that the main exothermic pathways were the reactions between oxidizing intermediates (NO, NO2), and reducing intermediates (CO, NH3).

# COMPUTATIONAL DETAILS

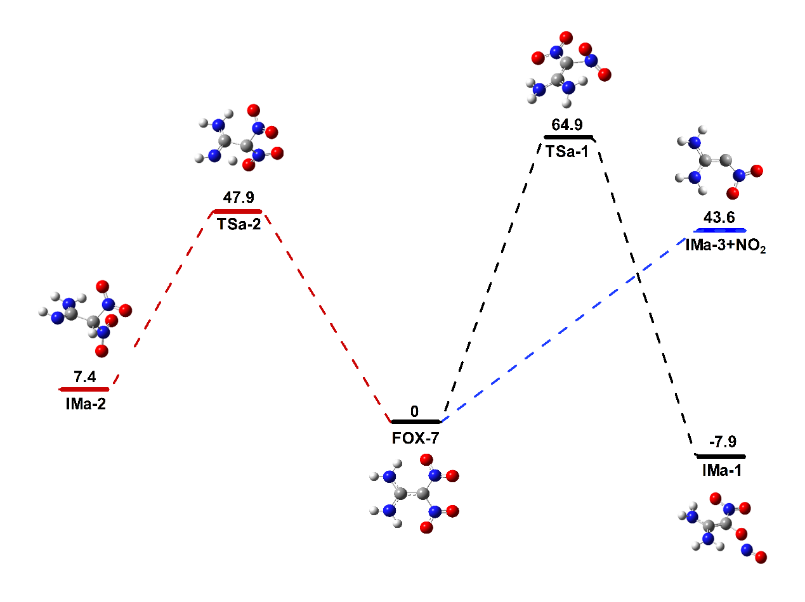
All density functional theory (DFT) calculations were accomplished by using the Gaussian 16 software package15 suite. The M06-2X functional was used and the basis set TZVP was adopted16-17. Vibrational frequencies analyses were performed at the same level of theory to confirm that all optimized structures are true local minima without imaginary frequency or transition state with only one imaginary frequency. Intrinsic reaction coordinate (IRC) was calculated on all transition states to guarantee that the transition structure connecting the reactants and products.

# RESULTS AND DISCUSSION

The structure of FOX-7 and the identifiers of all atoms are shown in Figure 1. The M06-2X/TZVP computed Gibbs free energy proﬁles of the three initial dissociation channels of isolated FOX-7 at the temperature of 600 K are showed in Figure 2. Since the cleavage of C-NO2 possesses the lowest energy barrier among the three dissociation channels, the NO2 should be one of the major products of FOX-7 dissociation (as shown by the blue line in Figure 2). The result also shows that it is appropriate to choose 600 K as the reaction temperature for the bimolecular reaction between NO2 and FOX-7. There are a great number of unreacted FOX-7 molecules in the system in the preliminary stage of isolated FOX-7 dissociation. Therefore, the NO2 product molecules are facile to react with the unreacted FOX-7 and resulting in new subsequent dissociation reactions. The following study emphasizes the possible bimolecular reactions between NO2 and FOX-7. All possible bimolecular reaction pathways were calculated at the temperature of 600 K and M06-2X/TZVP level.



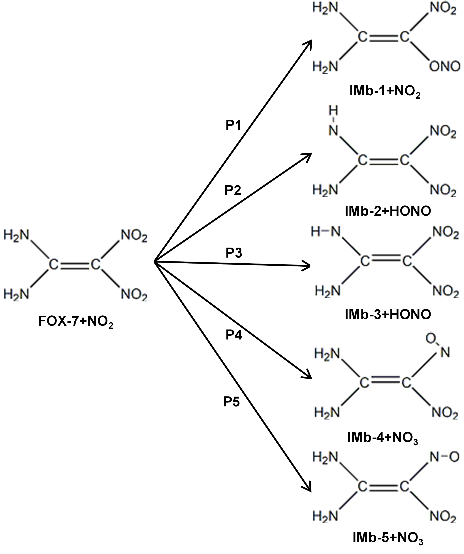
**Figure 1.** The structure of FOX-7 and identifiers of all atoms.



**Figure 2.** The computed Gibbs free energy profiles of the three main reaction paths of FOX-7 single-molecule dissociation: (1) NO2 elimination as shown by the blue line; (2) intermolecular hydrogen transfer as shown by the red line; (3) loss of No via a nitro-nitrite isomerization as shown by the black line. All values are given in kcal/mol.

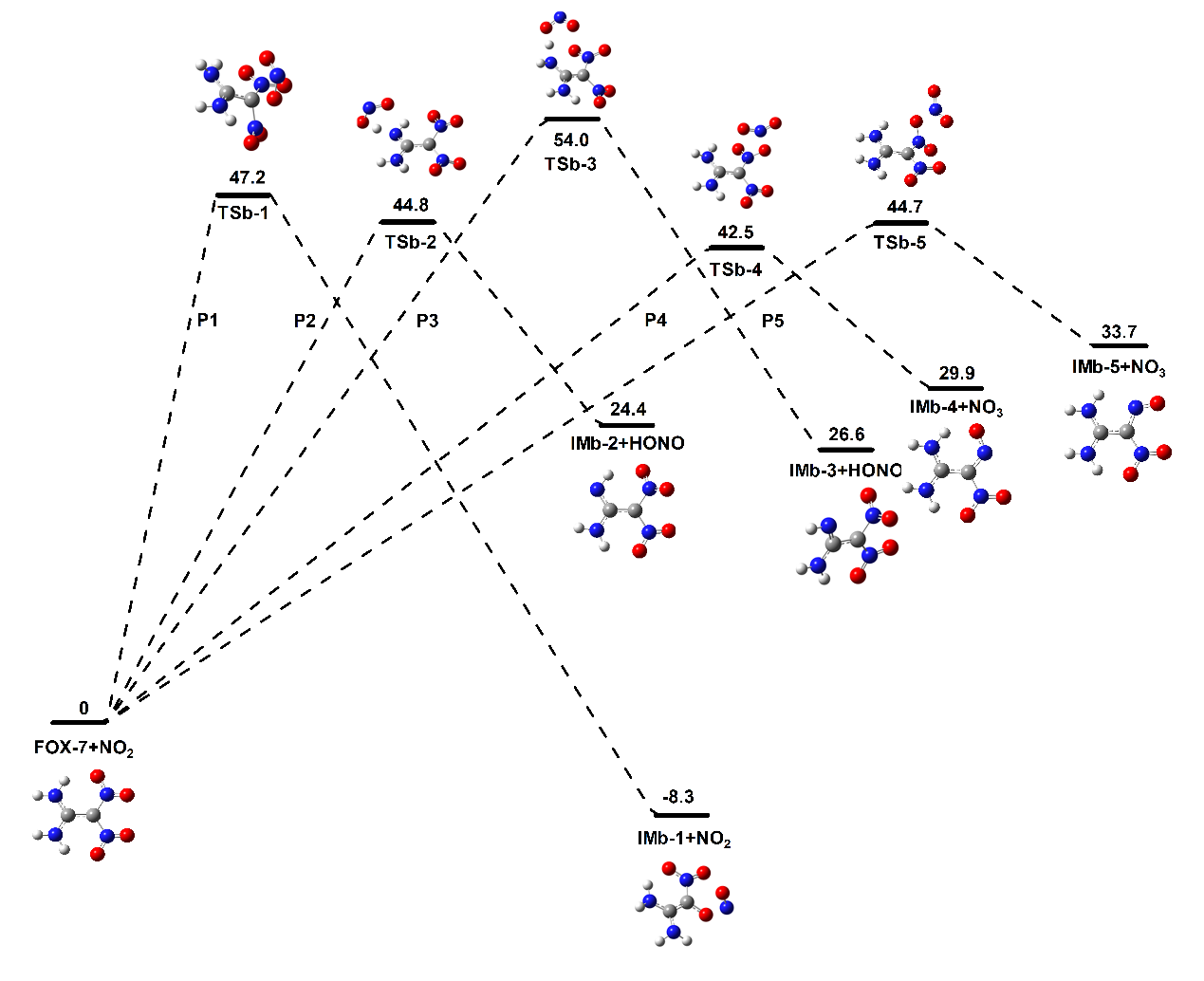
## The five initial thermal decomposition steps

The primary and subsequent steps in the decomposition of isolated FOX-7 are studied in the gas phase. As shown in Figure 3, five initial decomposition channels of FOX-7 and NO2 are obtained. The calculated Gibbs free energy (ΔG) profiles of five reaction paths are shown in Figure 4. Path P1 involves either of two O atoms of NO2 attacking 1C atom, which is bonded to the nitro groups of FOX-7. The energy barrier of path P1 is approximately 47.2 kcal/mol (TSb-1, as shown in Figure 4) and the products are IMb-1 and NO2. Paths P2 and P3 are both hydrogen abstraction reactions. O atom of NO2 seized 8H and 7H atoms of FOX-7, producing the intermediates IMb-2 and HONO or IMb-3 and HONO with energy barriers of 44.8 kcal/mol (TSb-2, as shown in Figure 4) and 54.0 kcal/mol (TSb-3, as shown in Figure 4), respectively. Paths P4 and P5 are oxygen abstraction reactions. The energy barriers of formation of IMb-4, IMb-5 and NO3 via attacking 10O and 11O atoms by O atom of NO2 are approximately 42.5 kcal/mol (TSb-4) and 44.7 kcal/mol (TSb-5), respectively. It should be noted that both intermediates IMb-4 and IMb-5 are closed-shell, which are relatively stable.



**Figure 3.** Five possible reaction channels for FOX-7 and NO2 bimolecular reaction.

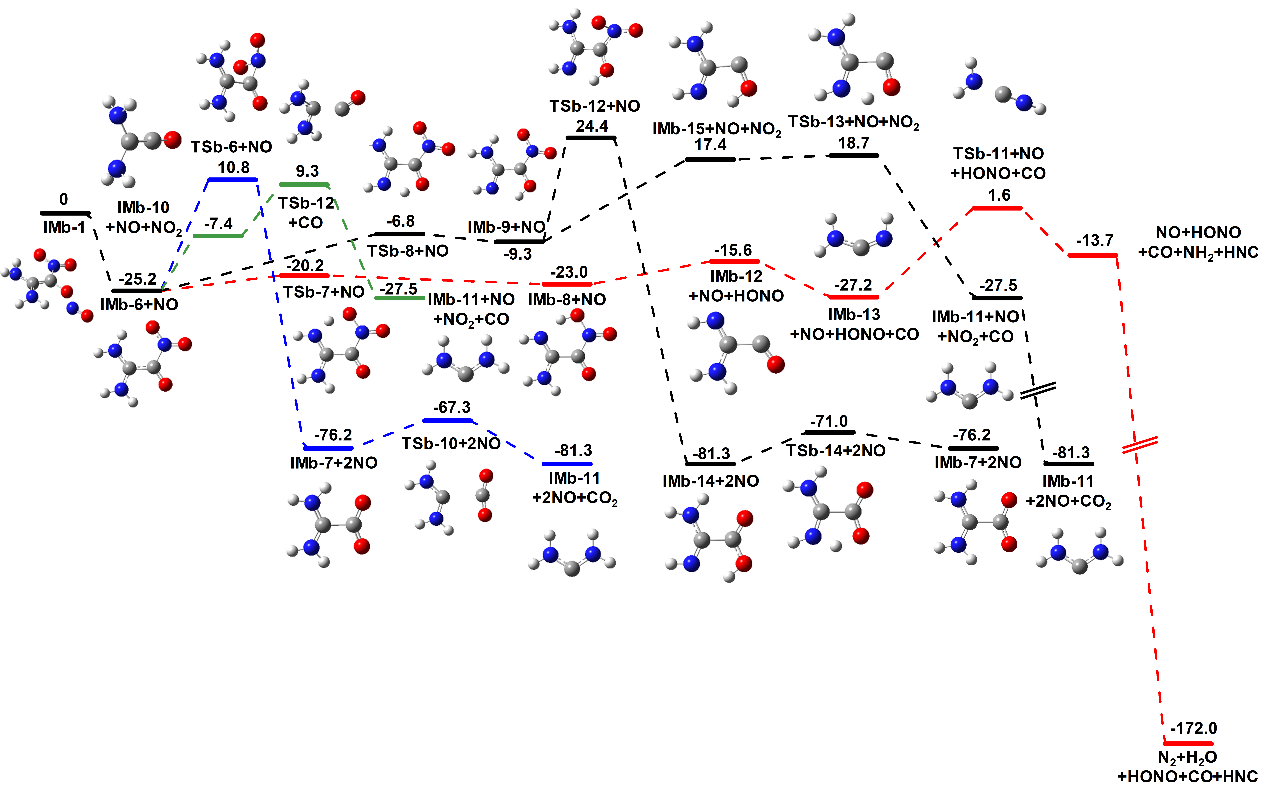
Therefore, the subsequent decomposition is difficult to occur due to the high activation barrier (as shown in Figure S1 and Figure S2, Supporting Information). Path P1 is dominant due to its strong chemical driving force and low transition state energy barrier. The most important possible initial step in FOX-7 decomposition is nitro-nitrite isomerization with a barrier of 58.4 kcal/mol at G4//B3LYP/6-311g (3df,2p)9 level or 64.9 kcal/mol at M06-2X/TZVP level in the present investigation in the gas phase. However, the formation of intermediate IMb-1 needs to overcome a lower barrier of 47.2 kcal/mol in FOX-7 and NO2 bimolecular reaction (path P1 as shown in Figure 3), which is the same as the IMa-1 (Figure 2). This suggests that NO2 catalyzes FOX-7 dissociation, which lowers profoundly the energy barrier of nitro isomerization, and the bimolecular reaction of FOX-7 and NO2 is an autocatalytic reaction, in which the channel P1 is dominant with a low energy barrier. This result is in accordance with the previous theoretical and experimental research that the concentration of the formed NO2 in FOX-7 dissociation increases first and then decreases11-13.



**Figure 4.** The computed Gibbs free energy profiles of possible initial dissociation channels of FOX-7 and NO2 bimolecular reaction. All values are given in kcal/mol.

## IMb-1 thermal decomposition steps

Each intermediate generated in FOX-7 and NO2 bimolecular reaction is further investigated. The loss of NO is the first reaction of the dissociation channel of IMb-1, which is spontaneous with no transition state and the products are IMb-6 and NO (as shown in Figure 5). Figure 5 shows four subsequent steps for the thermal decomposition of IMb-6. The first pathway is the loss of NO via nitro-nitrite isomerization to form IMb-7, with a barrier of 36.0 kcal/mol (as shown by the blue line in Figure 5). Both the second and the third pathways involve hydrogen shift, in which the hydrogen shifts from the amine group to the O atom of the nitro group producing IMb-8 (as shown by the red line in Figure 5), whereas the hydrogen shifts from the amine group to the O atom of carbonyl forming IMb-9 (as shown by the black line in Figure 5), with energy barriers of 18.4 kcal/mol (TSb-7) and 5.0 kcal/mol (TSb-8), respectively. The last one is the loss of NO2 via the cleavage of C−NO2 with a barrier of 17.8 kcal/mol (as shown by the green line in Figure 5). The most prone reaction channel is the hydrogen shift from the amine group to the O atom of the nitro group (as shown by the red line in Figure 5). IMb-7 encounters a C−C bond cleavage with an energy barrier of 8.9 kcal/mol (TSb-10), and yields IMb-11, NO, and CO2. IMb-8 loses HONO producing IMb-12 subsequently and then breaks the C−NH2 bond with a barrier of 28.8 kcal/mol (TSb-11) producing several fragments, such as NO, HONO, CO, NH2, and HCN. Noted that those fragments may undergo a series of reactions and form N2, H2O, HONO, CO, and HNC (details in Supporting Information Figure S3 and Figure S4, Supporting Information). It is worth mentioning that the computation results are in good agreement with previous MD simulation results11-12. IMb-9 undergoes two subsequent reaction steps: one is nitro-nitrite isomerization with a barrier of 33.7 kcal/mol (TSb-12) and the other one is the loss of NO2 with a barrier of 26.7 kcal/mol (TSb-15). The eventual products (IMb-11, NO, and CO2) of IMb-9 are the same as that of IMb-7. The subsequent decomposition channel of IMb-10 is the C−C bond cleavage with a barrier of 16.7 kcal/mol. Overall, our study reveals the dominant reaction path of IMb-1 thermal decomposition which is the lowest barrier path (as shown by the red line in Figure 5). It is noteworthy that IMb-10 has been detected in experiment 18.



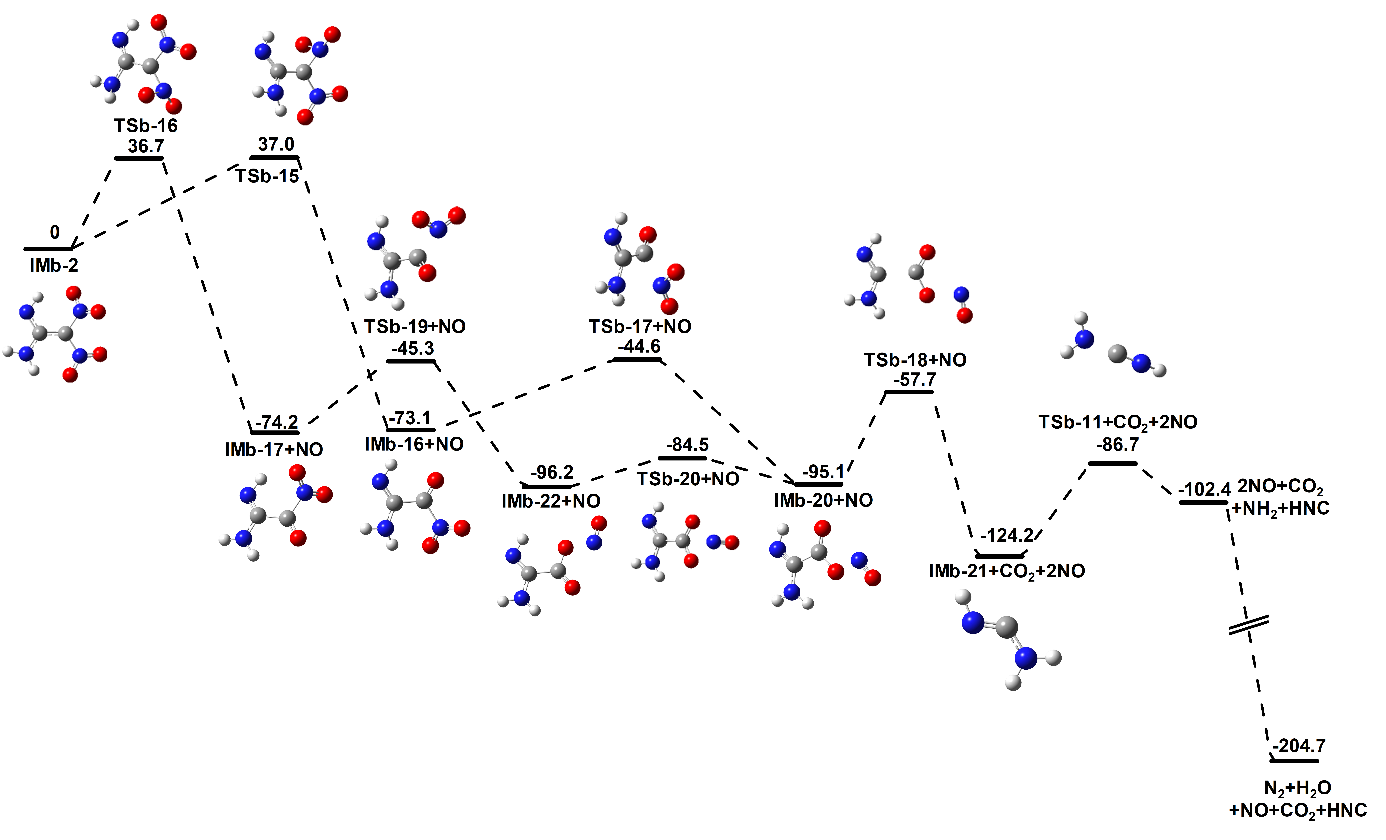
**Figure 5.** The computed Gibbs free energy profiles of possible dissociation channels of IMb-1. All values are given in kcal/mol.

## IMb-2 thermal decomposition steps

There are four possible initial dissociation pathways of IMb-2: two nitro-nitrite isomerization reactions and two bond cleavage reactions of different C−NO2, forming IMb-16, IMb-17, IMb-18, and IMb-19, respectively.

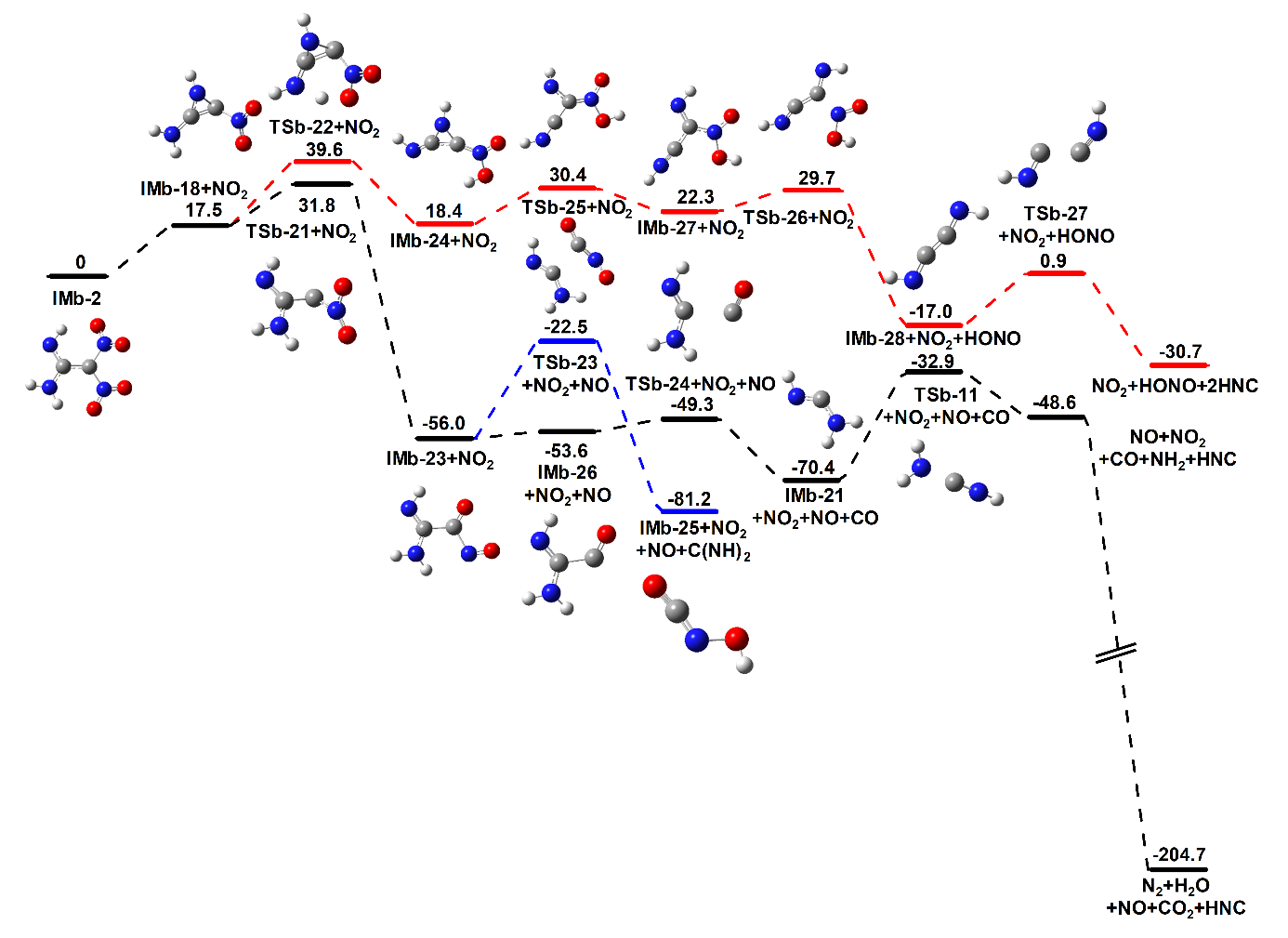
As shown in Figure 6, the barriers (TSb-15 and TSb-16) of two IMb-2 nitro isomerization reactions are 37.0 kcal/mol and 36.7 kcal/mol, and the intermediates are IMb-16 and IMb-17, respectively. IMb-16 and IMb-17 will lose the NO with an energy barrier of 28.5 kcal/mol (TSb-17) and 28.9 kcal/mol (TSb-19) and yield intermediates IMb-20 and IMb-22, respectively. IMb-22 transforms into IMb-20 with a barrier of 11.7 kcal/mol (TSb-20). IMb-21 is formed by the cleavage of C−C bond with a barrier of 37.4 kcal/mol (TSb-11) and the subsequent elimination of NH2. IMb-21 splits into five molecules: two NO molecules, CO2, HNC, and NH2. The subsequent reactions between product fragments (details in Figure S3 and Figure S4, Supporting Information) are embodied as well.

As Figure 7 showed, the formation of IMb-18 via C−NO2 bond cleavage possesses 17.5 kcal/mol increase in Gibbs free energy. IMb-18 undergoes two subsequent reaction steps: one involves the hydrogen atom shifting from amine to the nitro group to form IMb-24 with a barrier of 22.1 kcal/mol (TSb-22) (as shown by the red line in Figure 7); the other one is nitro-nitrite isomerization, yielding IMb-23 with a barrier of 14.3 kcal/mol via transition state TSb-21 (as shown by the black line in Figure 7). After the hydrogen shift of IMb-18, IMb-24 undergoes the cleavage of the C−NH bond and yields an isomer of IMb-27 with a barrier of 12 kcal/mol. HNC and HONO are formed via cleavage of C−N and C=C, the barrier of the transition state (TSb-27) for breaking the C=C bond is 17.9 kcal/mol. The resulting radical IMb-23 can undergo two subsequent steps: the pathway with the lowest barrier is the formation of IMb-26 with a barrier of 2.4 kcal/mol via the cleavage of C−NO bond and followed by the cleavage of C−C to form IMb-21 (as shown in Figure 6).

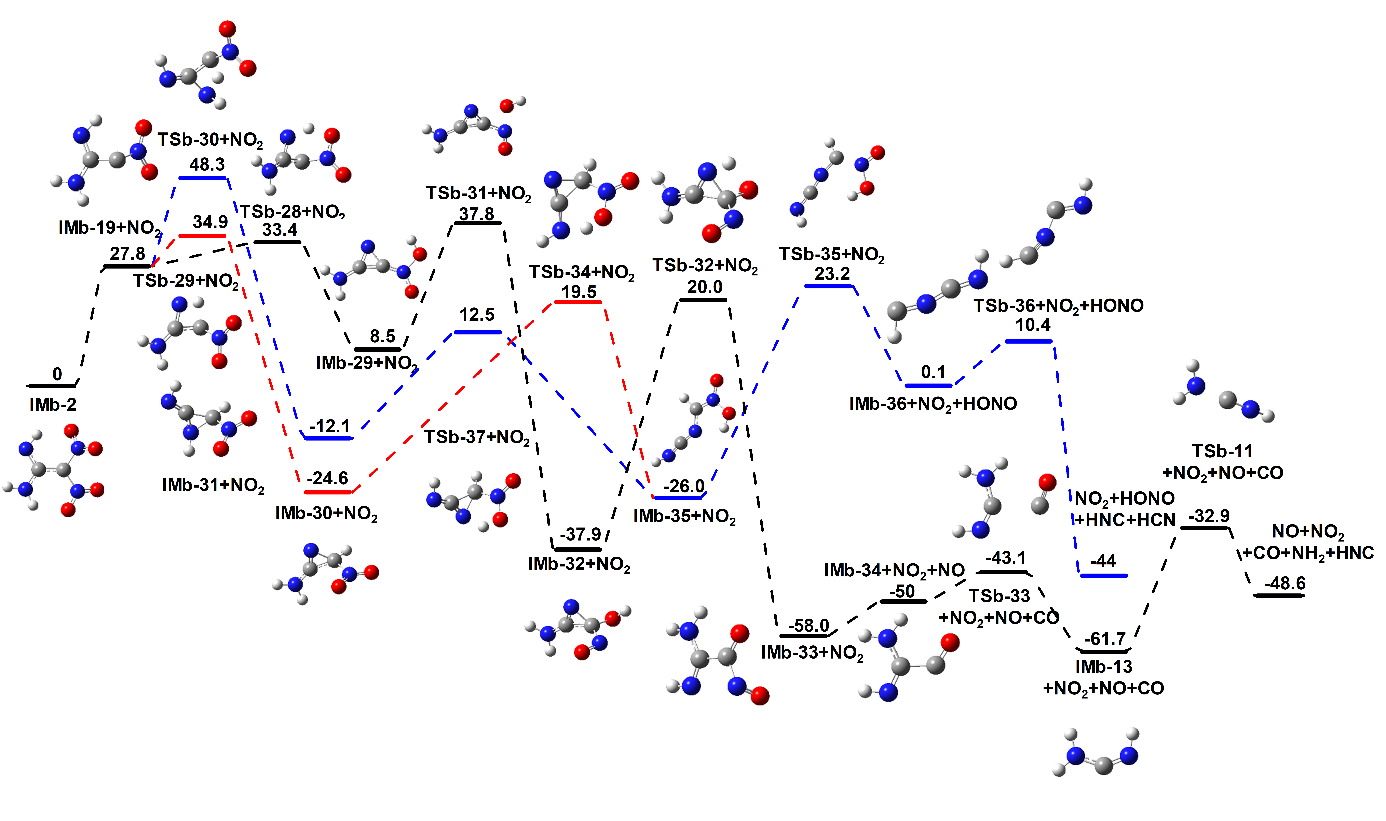


**Figure 6.** The computed Gibbs free energy profiles of possible dissociation channels of IMb-2. All values are given in kcal/mol.

Another intermediate IMb-19 is formed by the cleavage of the C−NO2 bond with Gibbs free energy increasing by 27.8 kcal/mol. The resulting radical species (IMb-19) will undergo three subsequent decomposition pathways involving H shifting from N to O of the nitro group (as shown by the black line in Figure 8), from N to C bonded to the nitro groups (as shown by the red line in Figure 8), and from amino group to C bonded to the nitro groups (as shown by the blue line in Figure 8), yielding IMb-29, IMb-30 and IMb-31 with the barrier of 5.6, 7.1 and 20.5 kcal/mol, respectively. IMb-35 is formed by a second H shift of IMb-30 and IMb-31, then followed by losing of HONO and cleavage of the carbon-nitrogen double bond. Despite the apparent double bond between the carbon and nitrogen the transition state (TSb-36) to break the C=N bond and form HNC and HCN is only 10.3 kcal/mol. After hydrogen transfers to the nitro groups in IMb-19, the shifting of OH is the main reaction with a barrier of 29.3 kcal/mol of IMb-29, forming species IMb-32 followed by a second H shift, loss of NO and cleavage of C−C bond, yielding IMb-13 species (detailed in Figure 5), CO and NO. The reaction of fragments about IMb-13 is not shown in the picture due to the limitation of image size.



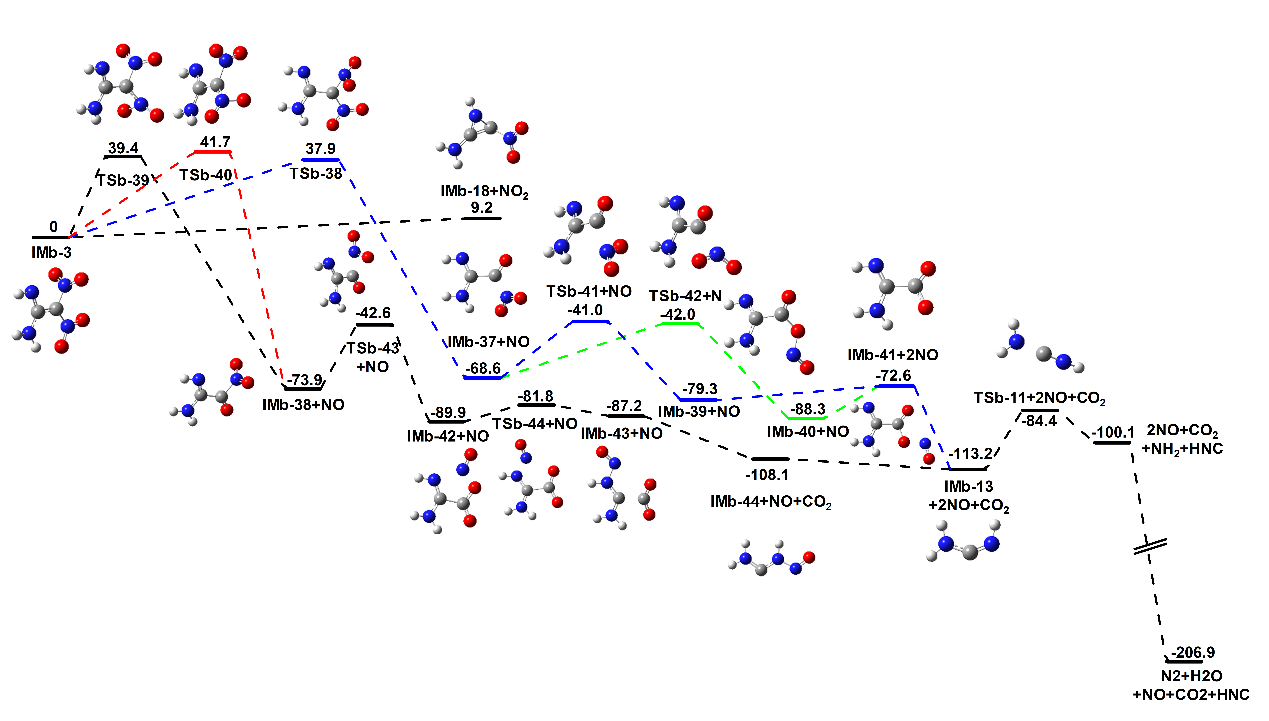
**Figure 7.** The computed Gibbs free energy profiles of possible dissociation channels of IMb-2. All values are given in kcal/mol.



**Figure 8.** The computed Gibbs free energy profiles of possible dissociation channels of IMb-2. All values are given in kcal/mol.

## IMb-3 thermal decomposition steps

There are four possible channels of IMb-3 thermal decomposition. The lowest barrier of 9.2 kcal/mol is the cleavage of C−NO2 bond yielding IMb-18, which has been discussed in the decomposition of IMb-2 (Figure 7). IMb-37 is formed via nitro-nitrite isomerization of IMb-3 with the barrier of 37.9 kcal/mol (TSb-38) and following by the secondary C−NO2 to CONO isomerization to form intermediate IMb-39 and IMb-40 (as shown by the blue line in Figure 9). Then they can form the same intermediate IMb-41 through the loss of NO. IMb-41 transfers into IMb-13 (discussed specifically in Figure 5) via cleavage of C-C bond. The other two channels are nitro isomerization of the same nitro group producing IMb-38. Noted that the structure and the energy of transition state TSb-39 (39.4 kcal/mol) and TSb-40 (41.7 kcal/mol) are only slightly different. A series of reactions lead to the conversion of IMb-38 into IMb-13 (as shown by the black line in Figure 9), including nitro isomerization, transfer of NO, cleavage C−C bond and loss of NO. According to our high-level calculations, the probabilities of products (N2, H2O, NO, CO2, and HNC) of the four channels are exactly the same. So far we have determined how the bimolecular reaction of FOX-7 and NO2 decomposed into stable fragments: N2, H2O, NO, CO2, HNC and HONO. Obviously, based on discussed computational results, IMb-13 and IMb-21 are important intermediates. Because once the FOX-7 decomposed into intermediates IMb-13 or IMb-21, which can easily completely decompose into small molecules.



**Figure 9.** The computed Gibbs free energy profiles of possible dissociation channels of IMb-3. All values are given in kcal/mol.

## Fragments Reaction

The main small molecule products are N2, H2O, NO, CO2, HONO, HNC and HCN. Clearly, these fragments can undergo collision and react with each other. Two possible reactions among these fragments are listed:

1.  19-20
2.  21

NO2 is an oxidizing agent, while CO is a reducing agent, NO2 and CO can react through an oxidation-reduction reaction and produce CO2 and NO with a barrier of 46.4 kcal/mol (detailed in Figure S3, Supporting Information). The net exothermic of this reaction is 57.1kcal/mol. The reaction of NH2 and NO is detailed in supporting information (Figure S4). The final products of this reaction are N2 and H2O. The total enthalpy of this reaction is -104.5 kcal/mol with a net exothermic of -107.4 kcal/mol.

Those two reactions have been studied in previous investigations. To better compare the exothermic process of both reactions, we recomputed the two reactions at the same M06-2X/TZVP level. Entropy and enthalpy changes for the two main fragments reactions are listed in Table 1.

|  |  |  |
| --- | --- | --- |
|  | ΔG(kcal/mol) | ΔH(kcal/mol) |
| NO2+CO---NO+CO2 | -53.8 | -57.1 |
| NH2+NO--- N2 +H2O | -104.5 | -107.4 |

**Table 1.** The calculated Relative Gibbs free energy and Enthalpy changes of the two fragments reactions. All values are given in kcal/mol.

Apart from Gibbs free energies, we calculated the relative enthalpies for all channels at the temperature at 600 K. For clarity, Table 2 lists Gibbs free energy and enthalpy of all possible products of each path. Combining with the reactions of fragments, the final products N2, H2O, NO, CO2, HNC, and HONO are produced by three reaction paths with the enthalpy of -180.3 kcal/mol and exothermic of 98.0 kcal/mol. The Gibbs free energy and enthalpy changes of FOX-7 and NO2 without fragments reaction is shown in supporting information (seen in Table.S1). In comparison, it indicates that energy changes caused by fragments collision dominate the bimolecular reaction.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reactants | Intermediate Product | ΔG | ΔH | Final Product |
| FOX-7  +NO2 | IMb-1+NO2 | -180.3 | -98.0 | N2+H2O+NO+CO2+HNC+HONO |
| -89.5 | -20.7 | IM12+2NO+CO2+NO2 |
| IMb-2+ HONO | -180.3 | -98.0 | N2+H2O+NO+CO2+HNC+HONO |
| -7.3 | 53.0 | NO2+ 2HONO+2HNC |
| -24.8 | 40.9 | NO2 + HNC+HCN+2HONO |
| IMb-3+ HONO | -180.3 | -98.0 | N2+H2O+NO+CO2+HNC+HONO |

**Table 2.** The calculated Relative Gibbs free energy and Enthalpy changes of bimolecular reaction of FOX-7 and NO2. All values are given in kcal/mol

# CONCLUSION:

Five initial reaction channels for the bimolecular reaction of NO2 and FOX-7 are demonstrated. The products of the three more favorable reaction paths P1, P2, and P3 are almost the same: N2, H2O, NO, CO2, HONO, HNC, and HCN. The bimolecular reaction between NO2 and FOX-7 has a significant influence on the dissociation of FOX-7. NO2 is not only an important product of FOX-7 dissociation but also a catalyzer for dissociation of FOX-7 (NO2 autocatalytic reaction). Moreover, the calculated products can explain the forming process of dissociation intermediates observed in experiments (e.g. IMb-6). The exothermic mechanism of the bimolecular reaction is revealed. FOX-7 decomposes into individual fragments, then a series of reactions occur between those fragments and an exothermic process is accomplished. The reactions between fragments make a major contribution to the exothermic procedure of FOX-7 dissociation.

Herein, though we have studied the bimolecular reaction between FOX-7 and NO2 systematically, the dissociation mechanism of the possible bimolecular reaction of intermediates and various fragments are remained to be further investigated. It’s indispensable for the application of FOX-7 and a fully understanding of the mechanism of FOX-7 dissociation. Whether the theory that fragments reaction is the major exothermic step applies to all energetic materials is under investigation.

Acknowledgements

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