Application of Ab Initio Molecular Dynamics for A Priori Elucidation of the Mechanism in Unimolecular Decomposition: The Case of 5-Nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO)

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Abstract: We have tested a new and general approach for the theoretical study of unimolecular decomposition. By combining the power of the ab initio molecular dynamics (MD) and ab initio molecular orbital (MO) methods, our approach requires no prior experimental knowledge or intuitive assumptions about the decomposition. Instead, the reaction channels are first sampled theoretically by simulating a molecule at high temperature in a number of trajectories, using the density functional theory (DFT) based ab initio MD method with a planewave basis set and pseudopotentials. Each type of these channels is then further examined by well-established ab initio MO method to locate the energy barrier and transition structure and to verify the ab initio MD results. The power of such an approach is demonstrated in a case study for the complicated unimolecular thermal decomposition of NTO (5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one), with several interesting new features uncovered. The C–NO_2 homolysis is indeed the dominant channel at high temperature, while the departing NO_2 could capture a H atom from the NTO ring to form HONO, by either a concerted bond breaking mechanism or by a bimolecular reaction between the NO_2 group and the triazol ring. At lower temperature, the dissociation channels initiated by hydrogen migrations should be activated first. The channel with hydrogen migration followed by ring opening and then by HONO loss has an energy barrier of 38.0 kcal/mol at the rate-determining step, being the lowest among all the investigated dissociation paths and much lower than previously thought. The energy barrier for nitro–nitrite rearrangement is lower than that for the C–NO_2 homolysis but makes only a minor contribution due to the entropy factor. And the NTO ring could rupture in the two C–N bonds connected to the carbonyl carbon, and the energy barriers for such processes are only 2–4 kcal/mol higher than that for the C–NO_2 homolysis.

Introduction

The decomposition of NTO (5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one, Figure 1) is a good example of the challenges that one has to face to unravel the reaction mechanism for the thermal dissociation of a not very big molecule. Developed as a potential high-performance energetic material,[1,2] NTO was found to have high energy release on decomposition. Yet at the same time, it was relatively insensitive to mechanical shock and showed good thermal stability, which are desirable properties from a practical point of view. The decomposition of NTO has attracted much attention from both experimentalists[3–16] and theoreticians.[17–22]
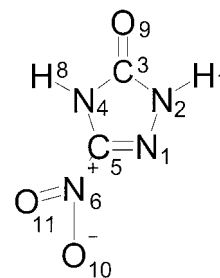

Figure 1. 5-Nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO) structure. The atom numbering scheme is followed throughout this paper.

Experimentally, many products were identified from the NTO decomposition, including NO, CO_2, N_2O, HCN, HNCO, and

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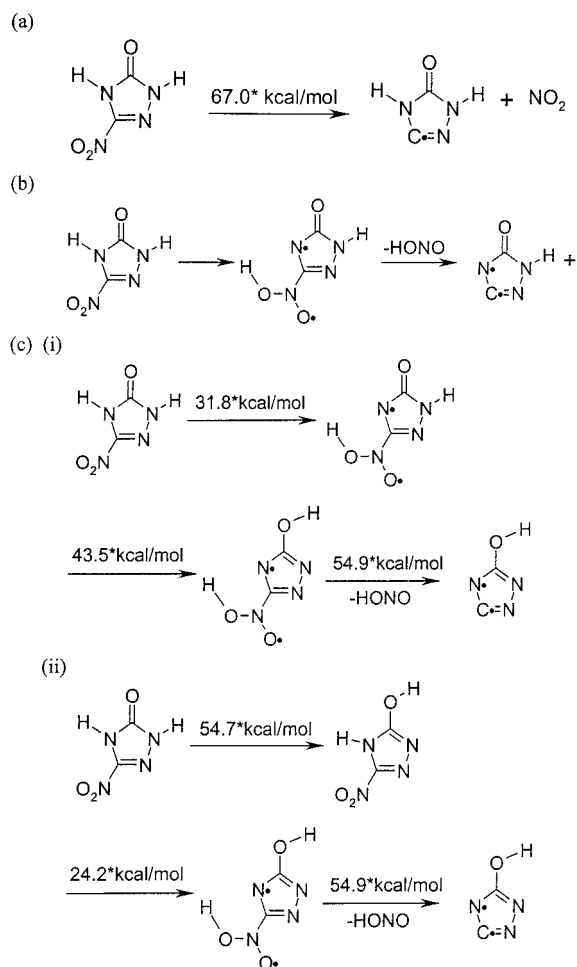
(a)

67.0* kcal/mol

(b)

−HONO

(c) (i)

31.8* kcal/mol

43.5* kcal/mol   54.9* kcal/mol
−HONO

(ii)

54.7* kcal/mol

24.2* kcal/mol   54.9* kcal/mol
−HONO

Figure 2. Previously proposed mechanism, with reaction barrier indicated with an asterisk: (a) $C-NO_2$ homolysis from ref 19; (b) hydrogen migration followed by HONO loss from ref 19; (c) the two reaction paths with the lowest energy barrier from ref 20.

CO.[3] The dominant species could either be NO,[3] NO_2,[6,7] N_2,[8] or CO_2,[3,8,15] depending on the experimental conditions. Several possible mechanisms have been suggested, including a bimolecular mechanism that produced CO_2.[15,16] For the unimolecular dissociation, the $C-NO_2$ bond was identified as the weak link, as it was typical among nitroaromatic explosives.[23] The $C-NO_2$ homolysis, as shown in Figure 2a, was proposed as an important decomposition channel,[6,7] especially at high temperature.[8] The bond strength of $C-NO_2$ was found to be 61.1 kcal/mol at the B3LYP/6-311+G** level of density functional theory (DFT)[17] and 67 kcal/mol by a Hartree−Fock calculation with a double-ζ plus polarization basis set and with single and double excitation configuration interaction (CISD).[19] The production of HONO was also attributed to the breaking of C5−N6 bond, although it is preceded by a hydrogen transfer, as shown in Figure 2b.[6,8,19] The migration of hydrogen atoms (bonded to N2 and N4) to other groups around the ring has been demonstrated by deuterium kinetic isotope effect[9,10] and by theoretical calcula-

tions.[17,18] Harris and Lammertsma obtained the energy and structure for seven such tautomers.[17] In a recent study, Wang, Chen, and Lin[20] extended the calculation to the transition barriers for tautomerization, which ranged from 30 to 50 kcal/mol, considerably lower than that for the scission of $C-NO_2$. In addition, these authors performed a detailed and systematic study on the subsequent step to break the C5−N6 bond for various combination of the tautomerization paths. The result was a collection of 39 decomposition paths among 18 intermediates and 14 transition structures, an illustration of the complexity of the decomposition process.[20] The two reaction paths with the lowest energy barriers are shown in Figure 2c. Meredith, Russell, Mowrey, and McDonald considered a few other possible dissociation mechanisms, including the ring rupture at C3−N2 and the exchange of position between NO_2 and H8, and found that they were energetically unfavorable.[19] Finally, a nitro−nitrite rearrangement channel has long been suspected in the decomposition of nitroaromatic explosives[23] and suggested for the decomposition of NTO,[11] although it had not been followed up by any calculations.[19]

The development of the Hartree−Fock ab initio method and DFT method has now made it possible to calculate the energy barrier and transition structure in a chemical reaction to a high degree of accuracy.[24,25] However, such calculations require the prior identification of the elementary reactions and their products, which is either based on experimental results or on chemical intuition. For a molecule of the size of NTO, it becomes difficult to identify the elementary reactions from the large number of experimentally observed final products. At the same time, chemical intuition is also unreliable because the number of possible reaction channels increases dramatically with the increasing molecular size.[20] Thus the study on the decomposition of NTO is an example of a very general problem.

In this paper, we report a strategy to address this problem in the case of NTO by combining ab initio molecular dynamics (MD) method with the more traditional molecular orbital (MO) method. First, the elementary reactions involved in the complicated decomposition process are directly obtained from ab initio MD simulation, rather than from the uncertain experimental results or chemical intuition. A set of trajectories are collected by simulating an NTO molecule at 3000 K, using ab initio MD method,[26−30] in which the potential energy and forces are calculated at each MD step within the framework of DFT. Such simulation not only samples the reaction channels but also reveals the relative importance of these channels. Then each type of reactions is further examined by the established MO method to locate its transition structure and energy barrier, at a higher accuracy level. In this way, the mechanisms of unimolecular thermal decomposition of NTO are mapped out a priori. Previously, we have tested this approach in a small scale (32 trajectories) for the thermal dissociation of acetic acid,[31] the mechanisms of which are well understood.[31−34] With the

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Table 1. C−NO$_2$ Homolysis Channels[a]

Reaction Channel	Direct breaking of C-NO$_2$ bond mechanisms	Max. barrier height (kcal/mol)	Frequency
1		62.5	6
2		62.5	22
		Total	28

[a] The energy differences are in the unit of kcal/mol, and those values indicated with asterisks are reaction barriers. Frequencies are obtained by ab initio MD trajectories, and all energy barriers/differences obtained from DFT B3LYP calculations

increased size and complexity of NTO, we have extended the number of trajectories to 200. The results indicate that our approach is general and powerful enough to be widely applied for the elucidation of unimolecular dissociation mechanisms.

Computational Details

The principles of ab initio MD method have been documented in the literature[26−30] and will not be reproduced here. We use the VASP (Vienna ab initio simulation package), developed at the Institut für Theoretische Physik of the Technische Universität Wien,[35−38] for our trajectory studies. The NTO molecule is put in a cubic box with a length of 9 Å to imitate gas-phase conditions. A planewave basis set with a cutoff energy of 349.4 eV is used for the electron wave function, which is solved at each MD step by conjugate gradient minimization of the total electronic energy. The Perdew−Wang[39] gradient correction is added to the exchange-correlation functional.[40] For the core region, the optimized Vanderbilt ultrasoft pseudopotentials[41] supplied with the VASP package[42,43] are directly used for H, C, N, and O atoms.

For the trajectory study, an NTO molecule is first equilibrated at 2000 K for 10 ps with a time step of 0.5 fs, starting from the equilibrium geometry. The starting geometry for each of the 200 trajectories is randomly selected from this equilibration run and heated to 3000 K, as controlled by a Nosé−Hoover thermostat.[45,46] A trajectory is terminated after 2000 steps if no reaction takes place.

The deficiencies for such a study are obvious. On the DFT part, a larger box and higher cutoff energy for the planewave basis set would improve the accuracy. On the MD trajectory part, longer simulation time, both for the sampling of starting geometries and for the duration of each trajectory, would be essential if accurate branching ratio is needed. For our purpose of understanding the decomposition mechanism, these deficiencies are compensated by a separate set of calculations, using the conventional Gaussian-based molecular orbital method at an improved accuracy level to locate the reaction barrier and transition structure for each type of the reaction channels observed in the trajectory study. In essence, the trajectory study based on ab initio MD method provides the leads from first principles for the elucidation of the reaction mechanisms by ab initio MO method at a higher level.

Various levels of ab initio MO method have already been applied to the study of NTO.[17−19] Harris and Lammertsma performed DFT

calculations at the B3LYP/6-31+g* level for structure optimization and at the B3LYP/6-311+G** level for single point energy calculation.[17] They also compared the results with the MP2 calculations for NTO and with the QCISD(T) calculations for *aci*-nitromethane using similar basis sets. They found the DFT results to be quite satisfactory. In this study we use the DFT method as implemented in Gaussian 98[44] with a slightly smaller basis set B3LYP/6-31g(d) for structure optimization and a slightly larger basis set B3LYP/6-311+g(2d,p) for single point calculations. Vibrational frequencies are calculated to take account of the zero point energy and to identify the transition structures. The stationary structures are confirmed by all real frequencies, and the transition structures by the presence of one imaginary frequency. We have also tested the structure optimization with B3LYP/6-31g(d,p), with polarization functions on the hydrogen atoms, and the results are quite close to the B3LYP/6-31g(d).

Results and Discussions

Out of the 200 trajectories, 68 leads to reactions, as summarized in Tables 1−4.[47] They can be broadly divided into four

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Table 2. Hydrogen Transfer Initiated Channels[a]

Reaction Channel	Hydrogen transfer initiated mechanisms	Max. barrier height (kcal/mol)	Frequency
3		30.0	15
4		38.0	8
5		50.4	2
6		44.3	2
7		--	1
8		--	1
		Total	29

[a] Also see notes for Table 1.

main categories, in the order of their relative importance: direct breaking of C5−N6 bond; H8 to O11 hydrogen transfer; nitro−nitrite rearrangement; direct ring rupture. Each type of these reactions has further variations. In the following discussion, our focus will be on the initial steps of the decomposition, although the products from these steps would go further fragmentation.

C−NO₂ Homolysis. The importance of the C−NO₂ homolysis for NTO decomposition has long been recognized.[6−8] Our ab initio MD simulation found 22 trajectories for this process, more than any other reaction channels listed in Tables 1−4. DFT B3LYP/6-311+g(2d,p) calculation found an activation

energy of 62.5 kcal/mol, close to previous DFT result of 61.1 kcal/mol[17] but smaller than the CISD+Q result of 67 kcal/mol.[19]

There is a very interesting variation of this mechanism (channel 1, Table 1), in which the departing NO₂ group captures H8 to form HONO. This is in contrast to the previous expectation that HONO is produced soly by a H migration to the NO₂ group first and followed by the loss of HONO (Figure 2b). Two transition structures are found to account for such a process of direct HONO elimination, as shown in Figure 3. TS2 is for a concerted breaking of the C5−N6 and H8−N4 bonds through a five member ring structure with N6 in the NO₂ group tilted

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Table 3. Nitro—Nitrite Rearrangement Channel[a]

Reaction Channel	Nitro-nitrite rearrangement		Max. barrier height (kcal/mol)	Frequency
9	(structure) 58.6* / -7.0 → **20** (structure) -1.7 → **21** (structure) + NO		58.6	5
			Total	5

[a] Also see notes for Table 1.

Table 4. Direct Ring Rupture Channels

Reaction Channel	Direct ring rupture mechanisms	Max. barrier height (kcal/mol)	Frequency
10	**22** (structure) 67.8* / 50.1 → CO + **23** (structure) ; ↓ -361.8 ; CO + NO₂ + HNC + NNH (**24** **25**)	67.8	3
11	(structure) 65.4* / 17.5 → **26** (structure) ; ↓ 41.5 ; **27** + **28** (structures)	65.4	2
12	(structure) 67.5* / 31.2 → **29** (structure)	67.5	1
		Total	6

[a] Also see notes for Table 1.

out of the triazole plane. The same five member ring is also seen in TS3, another transition structure which accounts for the H8 migration from N4 to O11 and will be discussed later. The contrast between TS2 and TS3 is that for TS3 the NO₂ group lies in the plane of the triazol ring and is 19.3 kcal/mol lower in energy than TS2. Nonetheless, the energy barrier at 49.3 kcal/mol for such a direct HONO loss mechanism through TS2 is lower than the C—NO₂ homolysis energy of 62.5 kcal/mol, although direct HONO loss is observed only 6 times in our trajectory study, compared to 22 times for C—NO₂ homolysis, probably due to the entropy factor.

TS1 represents a stepwise mechanism for HONO loss, in which the C5—N6 bond is first broken through the C—NO₂ homolysis and the departing NO₂ then attacks H8 and capture it through TS1 as in a bimolecular process. This is similar to the nitro—nitrite rearrangement reaction in nitromethane, which also goes through C—NO₂ homolysis first and then forms the methyl nitrite.[48] The energy barrier relative to the dissociated triazole ring and free NO₂ is 19.7 kcal/mol. The energy

difference between TS1 and TS2 is 32.9 kcal/mol, and the observed direct HONO loss in gas-phase unimolecular dissociation should be attributed to the concerted bond breaking through TS2. However, for the dissociation process in the solid where there are lots of free NO₂ groups, the bimolecular process could play a significant role.

Hydrogen Migration. Hydrogen (H8) migration from N4 to O11 to form **8** (channels 3—6, Table 2) was not considered in Harris and Lammertsma's extensive study on NTO tautomers.[17] Meredith and co-workers first studied this process theoretically and found an energy difference between **1** and **8** to be around 45 kcal/mol.[19] They argued that **8** was a biradical and its stable state should be a triplet. Thus H8 to O11 migration was thought to be spin-forbidden and the barrier was estimated to be higher than 45 kcal/mol. More recently, in a systematic study on the hydrogen migration paths, Wang, Chen, and Lin identified the energy barrier for H8 to O11 migration to be only 31.8 kcal/mol at the MP2/6-31G** level.[20] Since these authors
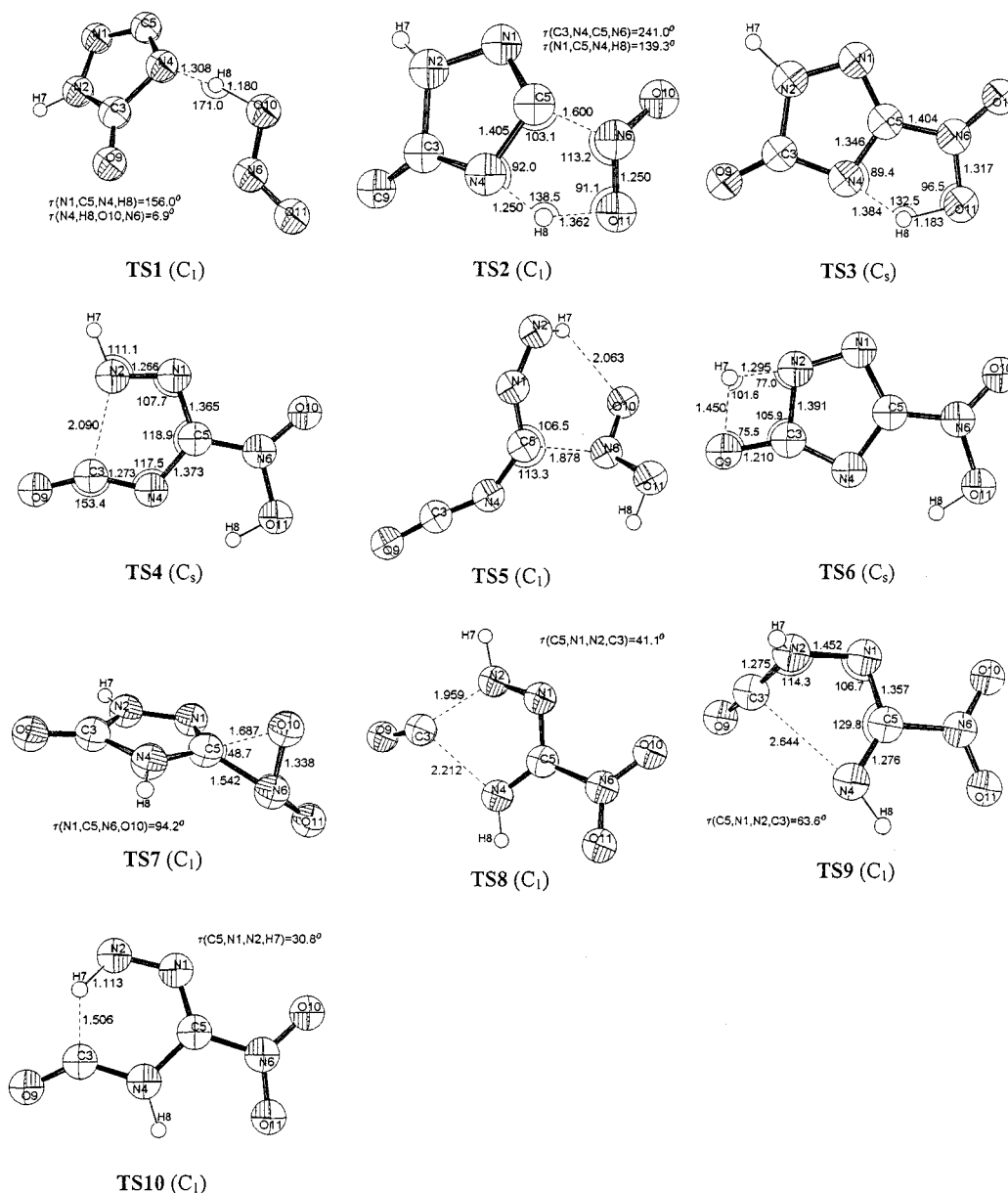
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Figure 3. Transition structures (also see Tables 1−4): TS1 for **2** + **3** → **4** + **5** as a bimolecular process; TS2 for concerted HONO elimination in channel 1; TS3 for channel 3; TS4 for the ring-opening step **8** → **9**; TS5 for loss of HONO from **9**; TS6 for the formation of **13**; TS7 for nitro−nitrite rearrangement in channel 9; TS8 for concerted ring rupture of C3−N4 and C3−N2 bonds; TS9 for ring rupture through C3−N4 bond; TS10 for ring rupture through C3−N2 bond. The unit for bond lengths is Å, and the unit for angles is deg.

did not mention spin states at all, it is most likely that their results were based on singlet states. According to our calculation at the B3LYP/6-311+g(2d,p) level, the energy difference between **8** and NTO (**1**) is 38.4 kcal/mol for triplet **8** and 27.7 kcal/mol for singlet **8**. Thus the singlet state is more stable than the triplet. The energy barrier for H8 to O11 migration in the singlet state is found to be 30.0 kcal/mol, in good agreement with Wang, Chen, and Lin's result of 31.8 kcal/mol.[20] Geometry optimization for NTO finds the molecule to be almost planar, and the same is true for **8**. The delocalized π bonding among the C, N, and O atoms makes the singlet a more stable state. The transition structure (TS3 in Figure 3) is also planar.

The significance of Wang, Chen, and Lin's work[20] is that among the hydrogen migration channels H8 to O11 migration at 31.8 kcal/mol has the lowest energy barrier. The energy barrier for the next channel, H8 to O9 migration (Figure 1), is 20 kcal/mol higher at 51.8 kcal/mol.[20] It means that H8 to O11

migration should be the dominant channel for tautomerization caused by H migration. This is indeed bore out in our trajectory calculation. A total of 29 trajectories were found to go through hydrogen migration, among which 27 had H8 to O11 migration as the initial step (channels 3−6, Table 2).

Systematic as their work was, Wang, Chen, and Lin focused their attention on the breaking of C5−N6 bond as the next step of decomposition.[20] Their extensive search turned up two paths with the least energy barrier as shown in Figure 2, which had a barrier of 54.9 kcal/mol at the rate-determining step. These paths are not observed in our trajectory calculations at all. Channel 4 in Table 2 is the most frequently observed decomposition channel after H migration, and it is a two-step process. First the ring opens at the C3−N2 bond through TS4 (in Figure 3) to form **9**. The C3−N2 distance in TS4 is at 2.09 Å, compared to the corresponding distance of 1.40 Å for NTO (**1**) and 1.48 Å for **8**. The process is slightly endothermic, with an energy

difference of 4.4 kcal/mol and a reaction barrier of 6.2 kcal/mol. The next decomposition step sees the breaking of the C5−N6 bond and the loss of HONO, while the ring opened further. The energy barrier at 38.0 kcal/mol is much lower than the mechanisms shown in Figure 2c, and the transition structure is shown in Figure 3 as TS5.

The other observed decomposition channels involve the breakup of the HONO group in radical dissociation, as shown for channels 5 and 6. To our best knowledge, these channels have not been considered before, as the attention is usually focused on the loss of HONO. The energy barriers for these two reaction paths are higher than that for channel 4 but lower than those shown in Figure 2c. In addition, 17 trajectories as in channels 3, 7, and 8 only go through hydrogen migration with no further dissociation, partly due to the fact that our simulation time is not long enough. These processes have been studied in great details in ref 20. The comparison between the Wang−Chen−Lin results and our present results shows that for a molecule as complex as NTO the ab initio MD-based trajectory calculation is superior to the extensive and systematic search based on chemical intuition in the search for important decomposition channels.

Nitro−Nitrite Rearrangement. Nitro−nitrite rearrangement as an initial decomposition step was first suggested for NTO by McMillen and co-workers,[11] but to our knowledge it has not been followed up by any theoretical studies. In our study, this reaction is observed in five trajectories (channel 9, Table 3). In the transition structure (TS7, Figure 3) for this reaction, the NO_2 group is rotated along the C5−N6 bond with the NO_2 plane being perpendicular to the NTO plane and an oxygen atom on NO_2 inserting into the C5−N6 bond. The energy barrier at 58.6 kcal/mol is 3.9 kcal/mol lower than that for C−NO_2 homolysis. TS7 is similar to the transition structure obtained by Turner and Davis[49] for the nitro−nitrite rearrangement in 1-nitropropene but rather different from that for nitromethane,[48] which goes through dissociation first in a two-step mechanism. The difference may be due to the fact that, in NTO and 1-nitropropene, NO_2 is bonded to a planar group with π bond, while, in nitromethane, NO_2 is bonded to a methyl group which makes the insertion of the oxygen atom into C−N bond difficult due to steric repulsion. After the rearrangement, further dissociation of the NO group is barrierless.

Direct Ring Rupture. The three types of reactions discussed so far all involved the NO_2 group in the first decomposition step (with the minor exception of channels 7 and 8). In this regard, channels 10−12 as listed in Table 4 belong to a distinct group because the first step for these reactions is the direct rupture of the NTO ring. The weak link in the NTO ring is the two C−N bonds connected to the carbonyl group, C3−N2 and C3−N4. These two bonds could rupture individually, as in channels 11 and 12 (TS9 and TS10 in Figure 3). They could also rupture simultaneously as in channel 10, with the two C−N bond breaking in a concerted way as shown in TS8, Figure 3, and with an energy barrier only slightly higher than the barrier for channel 11 or 12. The observation frequencies for all three channels are too low in our trajectory study to read much statistical significance and to judge their relative importance. However, in terms of reaction barrier, the activation energies for these channels are only 2−4 kcal/mol higher than the C−NO_2 homolysis, and as a result, they should be present during the decomposition process, especially at high temperature. None of these channels have been considered before, except for channel 12, which was suggested to explain the production of

CO_2.[14,19] Meredith and co-workers again limited themselves to the triplet state in their theoretical study on the rupture C3−N2 bond, the first step of channel 12. They found an energy barrier 17 kcal/mol higher than C−NO_2 homolysis, and the reaction was thus considered energetically unfavorable.[19] Our calculations of the reaction barriers for channels 10−12 are all done in the singlet state.

The frequency for various reaction channels obtained from our trajectory studies does not always correspond to the channel with the lowest energy barrier. In fact the frequency of C−NO_2 homolysis is much higher than all the other reaction channels although its energy barrier is substantially higher than that for the direct HONO loss or various H migration initiated channels. The energy barriers for nitro−nitrite and direct ring rupture channels are also close to the barrier for the C−NO_2 homolysis channel. This interesting observation can be attributed to the entropy factor. Using the nitro−nitrite rearrangement channel as an example, it requires first a rotation of the NO_2 group and then an oxygen atom tilting toward C5, according to the transition structure (TS7). While for the C−NO_2 homolysis, all it requires is the stretching vibration of C5−N6 bond. During a 10 ps ab initio MD simulation of NTO at 2000 K, the C5−N6 bond distance fluctuates an average of 10% of the equilibrium C5−N6 distance due to the stretching vibration, the largest among all bonds in NTO. Our simulation is performed at a temperature of 3000 K, and the entropy factor is expected to be important.

Conclusion

The combined ab initio MD and ab initio MO study has revealed three new mechanisms for NTO dissociation. First is the direct HONO loss mechanism either through a concerted breaking of C5−N6 and H8−N4 bonds or a bimolecular reaction between the departing NO_2 group and the triazole ring. Second is a path initiated by the H8 to O11 migration, followed by ring opening at C3−N2 and HONO loss. Finally, the NTO ring could rupture at the two C−N bonds connected to the carbonyl group, and the energy barriers for these channels are only 2−4 kcal/mol higher than the barrier for the C−NO_2 homolysis.

In addition, the nitro−nitrite rearrangement followed by the loss of NO group could also make a contribution to the NTO dissociation. Its activation barrier is slightly lower than that for the C−NO_2 homolysis.

Due to entropy factor, the dominant dissociation channel at high temperature should be the C−NO_2 homolysis, as indicated by the frequency of C−NO_2 homolysis in our trajectory study, which is much higher than any other channels, even though its energy barrier at 62.5 kcal/mol is higher than the hydrogen migration initiated channels and the direct HONO loss channel. At lower temperature, the H8 to O11 migration initiated decomposition processes would be the first activated channels due to the low activation barriers. Among these processes, channel 4, with ring opening after H migration and subsequent loss of HONO, has the lowest activation barrier, which is only 38.0 kcal/mol, significantly lower than previously thought.

Our study demonstrates the power of the combined ab initio MD and ab initio MO approach in elucidating the intricacy involved in unimolecular thermal decomposition. Such an approach should be generally applicable to the theoretical studies of thermal decomposition, without relying upon the prior knowledge or assumption of reaction products.

(49) Turner, A. G.; Davis, L. P. *J. Am. Chem. Soc.* **1984**, *106*, 5447.

Supporting Information Available: Tables and figures of geometrical parameters and vibration frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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