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Theoretical Study on the Reactions of the Cyclic Trinitrogen Radical toward Oxygen and Water

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Recently, the detection of the neutral simplest all-nitrogen ring, cyclic-N_3 radical, has been realized via various techniques, which has led to numerous studies on its structures, energetics, and spectroscopy. In particular, it has been postulated as a possible building block of high energy density materials. Yet, its intermolecular reactivity is poorly understood. In this paper, we for the first time studied the reactions of cyclic-N_3 with the widespread oxygen and water at the CCSD(T)/aug-cc-pVTZ //B3LYP/6-311++G(d,p)+ZPVE and G3B3//B3LYP/6-311++G(d,p) (italics) levels. An addition−elimination mechanism was revealed for the cyclic-N_3 + O_2 reaction that results in the elementary product $N_2 + NO + {}^3O$ with an overall barrier as high as 11.8 (*11.0*) kcal/mol. The calculated low rate constants (even at high temperatures) show that the cyclic-N_3 radical is stable against oxygen. The cyclic-N_3 + H_2O reaction is associated with a quasi H-abstraction mechanism forming the product cyclic-N_3H + OH with the rather high barrier of 35.7 (36.2) kcal/mol. This indicates that cyclic-N_3 is chemically inert toward H_2O. Chemical implications of the present work are discussed.

1. Introduction

In pure nitrogen compounds, their homonuclear single-bond energies are substantially less than one-third of their triple-bond and one-half of their double-bond energies. Therefore, a molecule containing N−N single-bond and double-bond may be metastable and to release energy when dissociating to N_2. As a result of this, all-nitrogen compounds have been conceived as candidates for high energy density materials (HEDMs) by chemists for the past decades.[1−5] Due to the highly thermodynamic instability of all-nitrogen species, the number of such known compounds is very limited. Therefore, their syntheses and handling present great challenges. Any spectroscopic and structural characterization of all-nitrogen molecules (ions) should be considered as a breakthrough in the cluster science.[4−15]

The simplest neutral all-nitrogen ring is the cyclic-N_3 radical. Although its isomer, linear-N_3, was already detected in 1956[16] and has received numerous experimental and theoretical investigations,[17−25] the report on the characterization of cyclic-N_3 is much limited. Early theoretical calculations predicted that the cyclic-N_3 radical is a doublet C_{2v} symmetric isomer.[26,27] Of particular interest, theoretical calculations by Bittererová et al.[28] suggested that through the barrierless exoergic recombination reaction N + cyclic-N_3 in the C_{3v} direction, cyclic-N_3 can be an alternative precursor to tetrahedral-N_4 (T_d), which has been believed to be the most strongly bound isomer of all-nitrogen clusters and has received rather extensive attention. Ab initio studies of unimolecular dissociation of cyclic-N_3 radical and the potential energy surface have been reported.[28,29] These investigations indicated that the cyclic-N_3 radical is stable against conversion to linear-N_3 and dissociation to N + N_2. Thus they reasonably proposed that cyclic-N_3 could be a stable azide isomer, and it would possess a long collision-free lifetime.

The first experimental indication for the possible existence of the cyclic-N_3 radical was provided by Hansen and Wodtke via the photolysis of ClN_3 at 235 nm, using velocity map imaging (VMI) technique in 2003.[11] In the subsequent mass spectrometric experiments, Wodtke and co-workers gave further support for the cyclic-N_3 via observation of two photoionization threshold energies using the time-of-flight (TOF) spectra.[12−14] Recently, Larson, Wodtke, and co-workers reported another photochemical route to cyclic-N_3 by a comprehensive study of the collision free photochemistry of methyl azide (CH_3N_3). They stated that methyl azide may be the most attractive photochemical precursor of cyclic-N_3 yet found.[15] Surely, other techniques (e.g., photoelectron spectroscopy, infrared spectroscopy) are still desired in future to afford a more detailed structural characterization of the interesting cyclic-N_3 radical.

The experimental detection, intrinsic stability against isomerization and dissociation as well as its potential application as a synthetic precursor to T_d-N_4 drive us to wonder about its chemical reactivity, which is very important to assess its capability as a building block in assembly. Thus, it is very desirable to explore the interaction of the cyclic-N_3 with various chemical species that might be encountered in assembly processes. It is well-known that transient radicals (O, H, OH, NCO, CN, etc.) can deplete many stable molecules, to say nothing of the cyclic-N_3 radical. The self-recombination reaction between the cyclic-N_3 radicals may also easily take place if its number density is high enough. So, for use of the cyclic-N_3 in assembly, the environmental atomic species must be removed as much as possible, and the number density of the cyclic-N_3 should be controlled. In this paper, we center on another respect, i.e., reactions of cyclic-N_3 with relatively stable molecular species, on which, to our knowledge, no previous reports have been reported. We for the first time studied the reactions of cyclic-N_3 radical with oxygen and water, both of which are key species in atmosphere and are usually difficult to be completely removed during the material manufacturing processes.

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TABLE 1: Relative Energies (kcal/mol) of the Reactants, Isomers, Transition States, and Products, and the $\|t_1\|$ Diagnostics for the Cyclic-N_3 + O_2 Reaction

species	B3LYP/ 6-311++G(d,p)	G3B3	CCSD(T)/ aug-cc-pVTZ+ZPVE	$\|t_1\|$
R cyclic-N_3 + O_2	0.0	0.0	0.0	
1	−0.3	−0.6	−0.4	0.018
2	6.1	3.3	4.2	0.034
3	6.5	5.3	6.1	
4	72.8			
5	−43.5	−43.1	−47.3	0.043
6	66.2			
TS1/2	6.5	9.5	3.5	0.037
TS1/3	8.5	11.4	7.3	
TS1/4	82.5	82.8	85.0	
TS2/3	8.8	6.6	7.2	
TS2/5	12.8	11.0	11.8	0.032
TS2/6	67.3			
TS5/P$_1$	−40.9	−49.1	−44.6	0.032
TS6/P$_2$	74.7			
P$_1$ N_2 + NO + ^3O	−54.0	−59.0	−59.8	
P$_2$ N_2 + N_2O	−86.8			

2. Theoretical Methods

For the cyclic-N_3 + O_2 and cyclic-N_3 + H_2O reaction systems, the optimized geometries and harmonic frequencies of the reactant, products, local minima, and transition states are obtained first at the B3LYP/6-31G(d) level. Connections of the transition states between designated local minima have been confirmed by intrinsic reaction coordinate (IRC) calculations at the B3LYP/6-31G(d) level. Subsequently, the calculation at the B3LYP/6-311++G(d,p) were used to check the geometries and frequencies of each isomer and transition state of the above two reaction systems. For both systems, single-point calculations are performed at the G3B3 and CCSD(T)/aug-cc-pVTZ levels at the B3LYP/6-311++G(d,p)-optimized geometries. The B3LYP/6-311++G(d,p) zero-point vibrational energies (ZPVE) are also included. All the geometrical and energetic calculations are carried out using the GAUSSIAN03 program package.[30] For better evaluation of the stability of the cyclic-N_3 radical against water and oxygen, the rate constants are calculated using the VKLab version 1.0.[31]

3. Results and Discussion

3.1. Reaction of Cyclic-N_3 + O_2. For cyclic-N_3 + O_2 reaction, the energies and crucial structures of the reactant, products, isomers and transition states are shown in Table 1 and Figure 1. The energy of reactant **R** cyclic-N_3 + O_2 is set at zero as a reference. By means of the inter-relation among the reactant, isomers, transition states, and products as well as the corresponding relative energies, the schematic profiles of the potential energy surfaces (PESs) are constructed as shown in Figure 2 based on the CCSD(T)/aug-cc-pVTZ// B3LYP/6-311++G(d,p) + ZPVE (in normal) (simplified as CCSD(T)//B3LYP), G3B3// B3LYP/6-311++G(d,p) (in italics) (simplified as G3//B3LYP) and B3LYP/6-311++G(d,p) (in parentheses) energetics. The symbol **TSm/n** is used to denote the transition state connecting the isomers **m** and **n**.

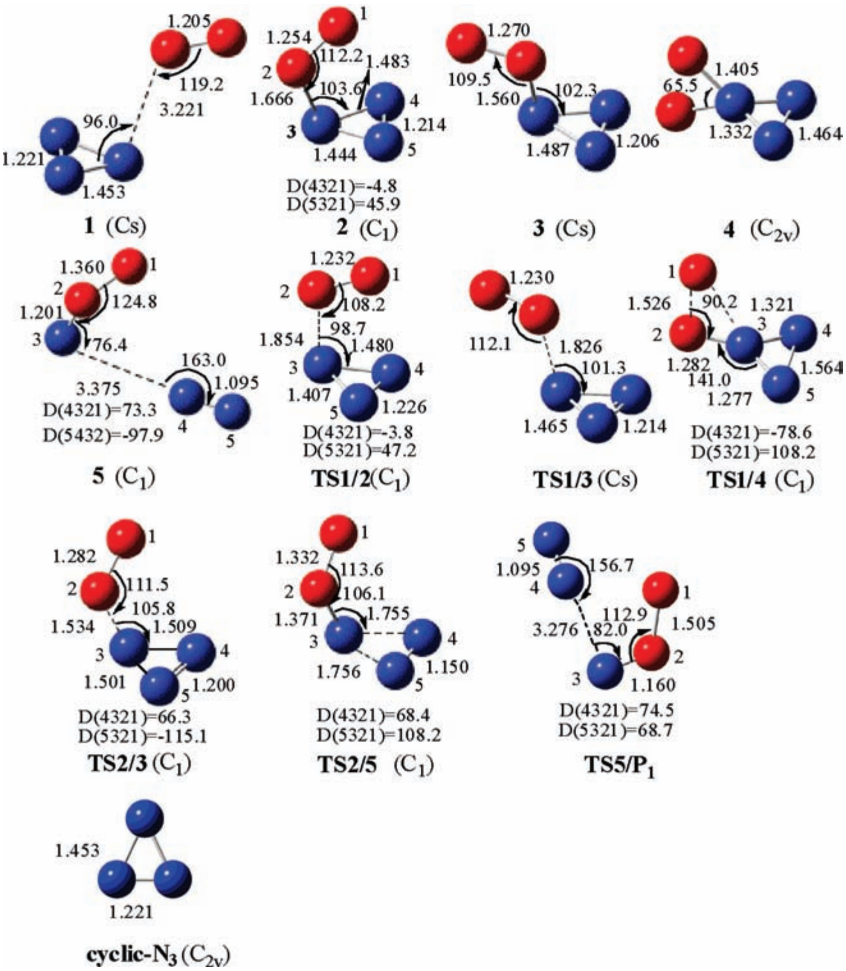

Figure 1. B3LYP/6-311++G(d,p)-optimized geometries for crucial reactant, isomers, transition states, and product in cyclic-N_3 + O_2 reaction. Bond lengths are in angstroms and angles in degrees.

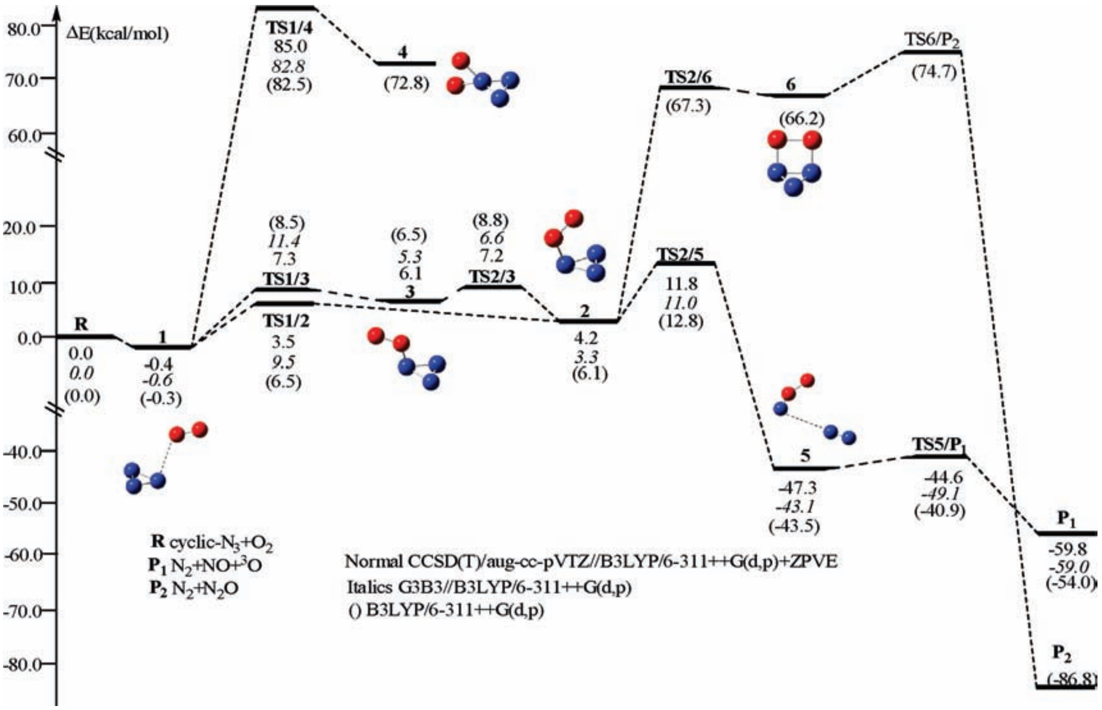

Figure 2. Schematic potential-energy surface of the cyclic-N_3 + O_2 reaction at the B3LYP/6-311++G(d,p) level (in parentheses) and the normal values and the italic values are the relative energies calculated at CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(d,p)+ZPVE and G3B3//B3LYP/6-311++G(d,p).

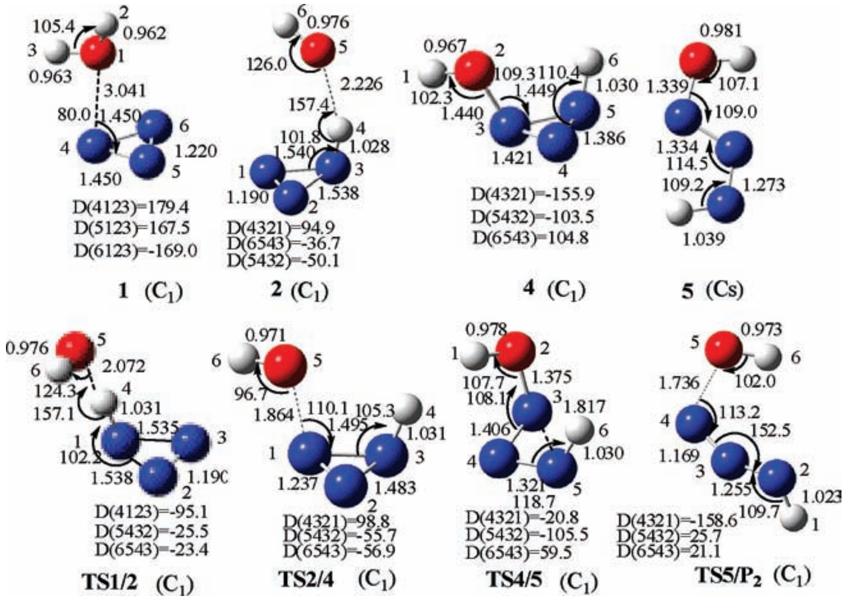

Figure 3. B3LYP/6-311++G(d,p)-optimized geometries for crucial reactant, isomers, transition states, and product in cyclic-N_3 + H_2O reaction. Bond lengths are in angstroms and angles in degrees.

As can be seen from Figure 2, the O atom attacks the N atom of the cyclic-N_3 radical above the plane and forms a radical−molecule complex **1** (−0.4, *−0.6* kcal/mol). The normal and italic values in parentheses are the relative energies calculated at the CCSD(T)//B3LYP and G3//B3LYP levels, respectively. Starting from **1**, three entrance channels have been located. Two of them are to form the addition isomers **2** and **3**, which are syn-trans isomerism, and another process is insertion of N atom to form isomer **4**. The barriers of conversion to **2** and **3** are 3.5 (*9.5*) kcal/mol and 7.3 (*11.4*) kcal/mol at the CCSD(T)//B3LYP (*G3//B3LYP*) levels. However the insertion process leading to the isomer **4** via **TS1/4** is kinetically much less competitive. The barrier for the conversion between isomers **2** and **3** is 4.2 (*3.3*) kcal/mol, so they may be concomitant. Subsequently, two transition states are located for isomer **2**. One is conversion to form a four-membered ring isomer **6** via **TS2/6**. The other conversion is N−N rupture with a barrier of 7.6 (*7.7*) kcal/mol to form complex **5**, which can be converted favorably to **P_1**N_2 + NO + ^{3}O (−59.8, *−59.0*) via **TS5/P_1** (−44.6, *−49.1*). Formation of low-lying **P_2** N_2 + N_2O via **TS6/P_2** is kinetically much less feasible. Further, we calculated the rate constants with the energies of CCSD(T) at 600 and 1000 K, and the pressures have been set at 760 Torr. It was found that the corresponding rate constants are rather low as 3.476×10^{-18} and 3.685×10^{-16} cm^3 molecule^{-1} s^{-1}. The above CCSD(T) results indicate that the reaction of cyclic-N_3 radical with O_2 is

TABLE 2: Relative Energies (kcal/mol) of the Reactants, Isomers, Transition States, and Products, and the $\|t_1\|$ Diagnostics for the Cyclic-N_3 + H_2O Reaction

species	B3LYP/ 6-311++G(d,p)	G3B3	CCSD(T)/aug-cc-pVTZ+ZPVE	$\|t_1\|$
R cyclic-N_3 + H_2O	0.0	0.0	0	
1	−1.8	−1.6	−1.4	0.016
2	33.1	33.6	34.2	0.015
3	31.2			
4	24.0	31.5	31.9	
5	−12.9	−2.2	−1.0	
6	15.5			
7	32.3			
8	−17.9			
9	−13.6			
TS1/2	33.2	33.7	34.1	0.024
TS1/3	64.1	79.2	76.6	
TS2/4	37.0	44.6	44.0	
TS4/5	43.0	46.7	47.5	
TS4/6	49.1			
TS4/7	60.4			
TS5/8	12.9			
TS5/P$_2$	0.9	13.4	14.9	
TS7/9	38.7			
P$_1$ cyclic-N_3H + OH	36.0	36.2	35.7	
P$_2$ HN_3 + OH	−9.5			

quite slow even at high temperatures, well indicative of its stability. For the relative energies of CCSD(T)//B3LYP and G3//B3LYP, significant deviations (around or larger than 4.0 kcal/mol) can be found for the species **5**, **TS1/2**, **TS1/3**, **TS5/P$_1$**, and especially for **TS1/2**, the deviation is up to 6.0 kcal/mol. **TS1/2** describes the association of the radical cyclic-N_3 and the other radical O_2, and this process may be influenced by the spin contamination. The spin contamination $\langle S^2 \rangle$ of **TS1/2** at the MP2G3large level in the G3B3 calculations is as large as 1.77, much larger than the standard value 0.75.

As a result, the most feasible channel on the [N_3O_2] PES can be written as **R** cyclic-N_3 + O_2 → **1** → **2** → **5** → **P$_1$** N_2 + NO + ^{3}O, and **R** cyclic-N_3+O_2 → **1** → **3** → **2** → **5** → **P$_1$** N_2 + NO + ^{3}O, and they are competitive. So, on the PES, the cyclic-N_3 + O_2 reaction leads to NO, ^{3}O, and N_2. The barrier of the determined process in this reaction is 11.8 (*11.0*) kcal/mol.

3.2. Reaction of Cyclic-N_3 + H_2O.

The structures of some crucial isomers and transition states are shown in Figure 3. The energies of the reactant, products, all isomers and transition states of cyclic-N_3 +H_2O reaction are shown in Table 2. The schematic profiles of the potential energy surfaces (PESs) are depicted as shown in Figure 4. The energy of reactant **R** cyclic-N_3 + H_2O is set at zero for reference.

Three types of attack reactions are identified as follows:

Path 1: H-abstraction: **R** cyclic-N_3 + H_2O → **1** → **2** → **P$_1$** cyclic-N_3H + OH.

Path 2: addition−elimination: **R** cyclic-N_3 + H_2O → **1** → **2** → **4** → **5** → **P$_2$** HN_3 + OH.

Path 3: insertion-elimination: **R** cyclic-N_3 + H_2O → **1** → **3**.

1 is a weakly bound radical−molecule complex H_2O···cyclic-N_3 that lies just −1.4 (*−1.6*) kcal/mol below the reactant **R** (0.0, *0.0*). **2** (34.2, *33.6* kcal/mol) is also a radical−molecule complex HO···cyclic-N_3H.[32] The rate-determining barriers for the three respective processes are 35.7 (*36.2*) kcal/mol, which is the direct energy difference between **P$_1$** and **R** in **Path 1**; 47.5 (*46.7*) kcal/mol via **TS4/5** in **Path 2**; and 76.6 (*79.2*) kcal/mol via **TS1/3** in **Path 3**. Clearly, we can find that the H-abstraction **Path 1** is kinetically the most competitive. It is worthy of note that if there is good cage effect, the departed fragments cyclic-N_3H and OH might recombination again to give the complex **1**.

So for all three channels, the barrier is too high to allow the reaction to take place at normal temperatures. Therefore, we could say that cyclic-N_3 is chemically inert toward H_2O. The fact that cyclic-N_3 is more reactive toward O_2 than H_2O is understandable since the triplet O_2 possesses both two radical sites and unsaturated π-bonds. The result of cyclic-N_3 + H_2O indicates that cyclic-N_3 is a weak atom-abstractor. So, we can infer that cyclic-N_3 might also be unreactive toward various closed-shell stable hydrides such as CH_4, NH_3, HF, etc. Surely, for the cyclic-N_3 radical, reactions with reactive transient radicals

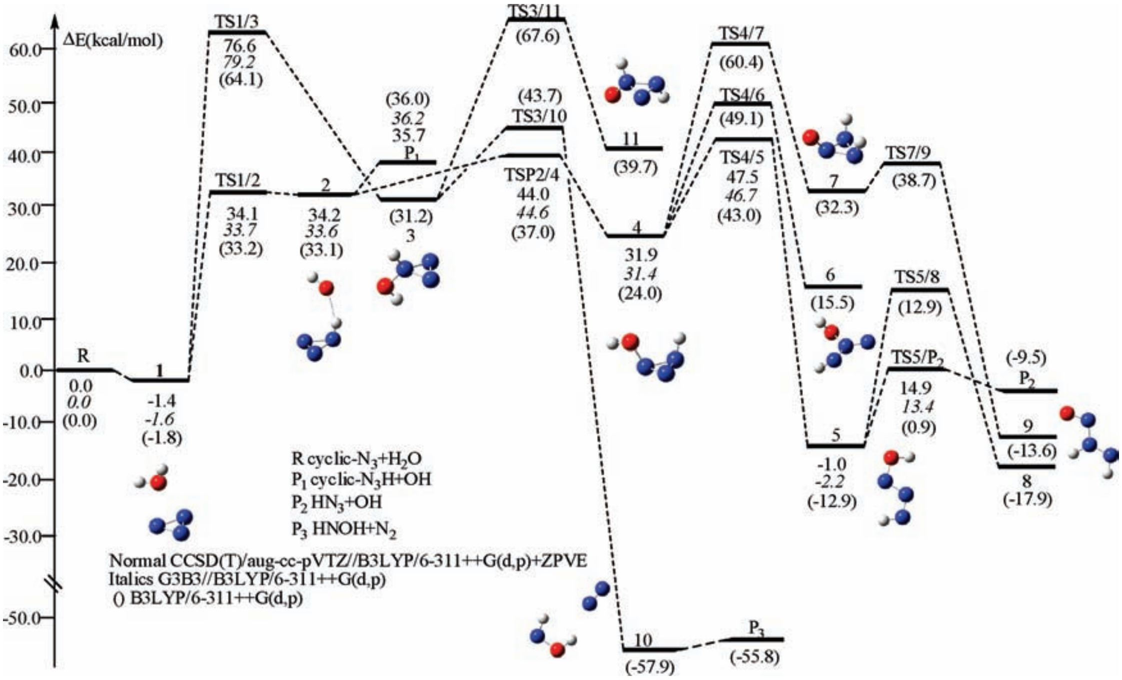

Figure 4. Schematic potential-energy surface of the cyclic-N_3 + H_2O reaction at the B3LYP/6-311++G(d,p) level (in parentheses) and the normal values and the italic values are the relative energies calculated at CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(d,p)+ZPVE and G3B3//B3LYP/6-311++G(d,p) levels, respectively.

as well as with itself (i.e., self-recombination) could be much faster. Certain refined conditions such as controllable temperature[33] and high dilution[34] would further suppress such radical−radical processes. Then, under these circumstances, we can say that the cyclic-N_3 radical can be stable in a moist environment and is even difficult to be oxidized by oxygen at relative low temperatures. We have been thinking of the ways to kinetically stabilize the cyclic-N_3 radical. When the cyclic-N_3 is directed for the potential use in assembly, the knowledge of its chemical reactivity toward various important environmental gases is thus very desirable and important. Our work represents the first attempt to study the interactions of cyclic-N_3 with relatively stable molecules.

3.3. Test Calculations. We are aware that during the cyclic-$N_3 + O_2$ reaction, the doublet radical (cyclic-N_3) interacts with the triplet biradical (O_2) to form the new doublet radical species ($[N_3O_2]$). So, we calculated the multiconfigurational nature of various intermediate species, as characterized by the T1 Diagnostics.[35,36] A value of $||t_1||$ higher than 0.02 indicates that the degree of multireference character is large enough to cast serious doubt on the reliability of single reference correlation treatments. As shown in Table 1, the six $||t_1||$ values in the CCSD(T) treatment with the aug-cc-pVTZ basis set are 0.018, 0.034, 0.043, 0.037, 0.032, and 0.032 for **1**, **2**, **5**, **TS1/2**, **TS2/5**, and **TS5/P$_1$**, respectively. Clearly, except for complex **1**, the cyclic-$N_3 + O_2$ reaction has a noticeable multireference effect. On the other hand, the calculated values of $||t_1||$ (see Table 2) of the species **1**, **2**, and **TS1/2** of the cyclic-$N_3 + H_2O$ reaction are 0.016, 0.015, and 0.024, respectively. Clearly, the cyclic-$N_3 + H_2O$ reaction is subject to less multireference effect than cyclic-$N_3 + O_2$.[37] Considering the large total barrier in cyclic-$N_3 + O_2$ and cyclic-$N_3 + H_2O$ reactions, we expect that the multiconfigurational effect would not change our basic conclusions.

4. Conclusion

To sum up, we computationally showed that the reactions cyclic-$N_3 + O_2$ and cyclic-$N_3 + H_2O$ proceed via considerable barriers. Detailed potential energy surfaces are established at the CCSD(T)//B3LYP and G3//B3LYP level. The results are summarized as follows:

(1) For the reaction cyclic-$N_3 + O_2$, the most feasible channel can be written as **R** cyclic-$N_3 + O_2 \rightarrow \mathbf{1} \rightarrow \mathbf{2} \rightarrow \mathbf{5} \rightarrow \mathbf{P_1}$ N_2 + NO + ^3O, and **R** cyclic-$N_3 + O_2 \rightarrow \mathbf{1} \rightarrow \mathbf{3} \rightarrow \mathbf{2} \rightarrow \mathbf{5} \rightarrow \mathbf{P_1}$ N_2 + NO + ^3O, and they are competitive. So the cyclic-$N_3 + O_2$ reaction leads to N_2, NO, and ^3O. This reaction proceeds via an addition−elimination mechanism. Owing that the barrier of the determined process in this reaction is 11.8 (*11.0*) kcal/mol, we consider that the cyclic-N_3 radical is stable against oxygen.

(2) For the reaction cyclic-$N_3 + H_2O$, the pathways can be deduced as **R** cyclic-$N_3 + H_2O \rightarrow \mathbf{1} \rightarrow \mathbf{2} \rightarrow \mathbf{P_1}$ cyclic-N_3H + OH. This reaction proceeds via a hydrogen abstraction mechanism with the rather high barrier of 35.7 (*36.2*) kcal/mol. This indicates that cyclic-N_3 is chemically inert toward H_2O.

The present results improve our understanding on the reactivity of the cyclic-N_3 radical. Future laboratory investigations on the cyclic-N_3 radical chemistry are expected.

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Supporting Information Available: Total (atomic units) energies of the reactants, isomers, transition states, and products have been shown. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) We should point out that HO···c-N_3H **2** has a small imaginary frequency−53.8 cm^{-1} corresponding to the wagging of O−H bond. We attempted to locate a similar structure with all real frequencies, yet failed. Any optimization leads to H_2O···cyclic-N_3 **1**. This suggests the rather high kinetic instability of **2** toward conversion to **1**. Luckily, the optimization

difficulty of **2** should not alter our conclusion that the overall H-abstraction barrier is 36.0 (*36.2*) kcal/mol, which is simply the energy difference between $\mathbf{P_1}$ c-N_3H + OH and **R** cyclic-N_3 + H_2O.

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