

ARTICLE

Theoretical Study on Dissociation Potential Energy Surface of Peroxynitric Acid

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The lowest energy structures of peroxynitric acid have been studied with B3LYP/6-311++G(2d,2p) method. The potential energy surfaces (PES) along the O–N and O–O bonds have been scanned at CCSD(T)/aug-cc-pVDZ level, respectively. The calculated results show that on the O–N PES, the O3–N4 bond length of the loose transition state is 2.82 Å and the corresponding energy barrier is 25.6 kcal/mol, while on the O–O PES, the loose transition state with of O2–O3 bond length of 2.35 Å has the energy barrier of 37.4 kcal/mol. Thus the primary reaction path for peroxynitric acid is the dissociation into HO₂ and NO₂.

Key words: Peroxynitric acid, Structure, Potential energy surface, Theoretical study

I. INTRODUCTION

As early as 1977, Niki *et al.* verified that peroxynitric acid (HO₂NO₂, PNA) is a molecule that forms from HO₂ and NO₂ [1]. HO₂NO₂ is an important species that acts as a gas-phase reservoir for odd HO_x (OH, HO₂) and odd NO_x (NO, NO₂) chemical families in the stratosphere and troposphere [2]. Scientists have carried out a lot of investigations on its dominant atmospheric loss processes, including thermal decomposition [3–6], photodissociation [7–13], and reaction with the OH radical [14, 15].

Zabel experimentally investigated the thermal decomposition rate constant of HO₂NO₂ as a function of temperature and pressure [3]. At B3LYP/6-311++G(3df,3pd) level, Staikova *et al.* calculated the stationary points on the lowest singlet and triplet potential energy surfaces (PES) of the HO₂NO₂ system [4]. And Gierczak *et al.* reported the rate coefficients for the gas-phase thermal decomposition of HO₂NO₂ at temperature between 331 and 350 K at the pressure of 25 Torr to 50 Torr of N₂ [5]. Furthermore, Szakács *et al.* computed the stable conformer and the corresponding heat of formation and entropy values of HO₂NO₂ by high-accuracy quantum chemical calculations [6]. However, the detailed potential surfaces for the dissociation of HO₂NO₂ into NO₂ or NO₃ have not been understood. Here we apply B3LYP/6-311++G(2d,2p) method to

study the structure of HO₂NO₂ and use CCSD(T)/aug-cc-pVDZ method to scan the PES along the O–N and O–O bonds for HO₂NO₂, in order to elucidate its dissociation mechanism.

II. COMPUTATIONAL DETAILS

The geometry optimization of the reactants is performed using Becke's three-parameter hybrid exchange functional [16] and the LYP [17, 18] correlation functional (B3LYP) in conjunction with the split valence polarized basis set 6-311++G(2d,2p). To improve the accuracy, the coupled-cluster theory CCSD(T) with the single, double, and triple excitations [19, 20] and the Dunning's correlation-consistent double- ζ basis set augmented with diffuse functions aug-cc-pVDZ [21] is used to scan the PES along the O–N and O–O bonds. All calculations are done with the Gaussian 09 package [22].

III. RESULTS AND DISCUSSION

A. Structures of HO₂NO₂

The lowest energy structures of HO₂NO₂ are a pair of mirror image isomers named as IS1 and IS2. Their optimized geometries are depicted in Fig.1 and the corresponding parameters are listed in Table I. From Table I we can see that almost all the bond lengths and bond angles in IS1 are the same as those in IS2, except the O3–N4 bond length. It is 1.516 Å in IS1, which is only 0.001 Å longer than that in IS2. The main difference

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TABLE I The geometric parameters for peroxyntic acid at B3LYP/6-311++G(2d,2p) level.

		IS1	IS2	Ref.[23] ^a	Ref.[24] ^b	Ref.[26] ^c
Bond length/(Å)	$R(\text{H1}-\text{O2})$	0.970	0.970	0.972	0.970	0.971
	$R(\text{O2}-\text{O3})$	1.400	1.400	1.399	1.401	1.414
	$R(\text{O3}-\text{N4})$	1.516	1.515	1.531	1.516	1.491
	$R(\text{N4}-\text{O5})$	1.190	1.190	1.189	1.190	1.195
	$R(\text{N4}-\text{O6})$	1.192	1.192	1.190	1.192	1.196
	Angle/(°)	$A(\text{H1O2O3})$	103.2	103.2	103.4	103.2
$A(\text{O2O3N4})$		109.6	109.6	109.6	109.6	108.7
$A(\text{O3N4O5})$		116.6	116.6	116.3	116.6	
$A(\text{O3N4O6})$		109.9	109.9	109.9	109.9	109.8
$A(\text{O5N4O6})$		133.5	133.5		133.8	133.3
Dihedral angle/(°)		$D(\text{H1O2O3N4})$	88.1	-88.1	90.3	88.1
	$D(\text{O2O3N4O5})$	-9.3	9.3		-9.3	-10.2
	$D(\text{O2O3N4O6})$	171.7	-171.7	171.1	171.8	178.5

^a B3LYP/6-311++G** level.

^b B3LYP/6-311++G(2d,2p) level.

^c CCSD(T)/aug-cc-pVTZ level.

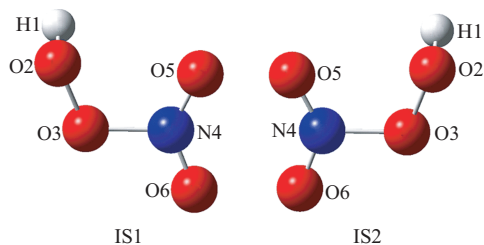


FIG. 1 Molecular structures of peroxyntic acid optimized by B3LYP/6-311++G(2d,2p) method.

between the structures of IS1 and IS2 is the dihedral angles. For example, the dihedral angle among H1, O2, O3, and N4 atoms is 88.1° in IS1, while it is -88.1° in IS2. And the dihedral angle among O2, O3, N4, and O5 atoms is -9.3° in IS1, while it is 9.3° in IS2. Similarly, other dihedral angles among the same four atoms in the structure of IS1 and IS2 have the same absolute values and opposite signs, respectively.

Using various levels of theory, including HF/6-311++G**, B3LYP/6-311++G**, QCISD/6-31G**, and MP2/6-311++G(2df,2pd), Chen and Hamilton [23] calculated the structure of HO_2NO_2 , and showed that when the similar basis sets were applied, the structure computed by B3LYP method was similar to that of Møller-Plessett perturbation theory (MP2) and quadratic configuration interaction theory with single and double substitution (QCISD). Then they draw the conclusion that for HO_2NO_2 the vibrational bands predicted by the B3LYP method were better than those by MP2 even with a large basis set, and was equal in quality to QCISD/6-31G**. We also list the geometric parameters for HO_2NO_2 reported in Refs.[23, 24,

26], as shown in Table I. From Table I we can see that the geometry of IS1 agrees very well with the structure of HO_2NO_2 reported by Chen and Hamilton [23]. They almost have the same bond lengths, bond angles, and dihedral angles, except the lengths of O3–N4 bond, which is 1.516 and 0.015 Å longer than that reported by Chen and Hamilton [23].

Aloisio and Francisco [24] also used B3LYP method and various basis sets to calculate the structure of HO_2NO_2 , and their calculated geometry for HO_2NO_2 was in good agreement with the structure calculated by Chen and Hamilton [23], as well as the experimental results by Suenram *et al.* [25]. Table I shows the same structure by B3LYP/6-311++G(2d,2p) method. Using CCSD(T)/aug-cc-pVTZ method, Matthews *et al.* [26] performed a high-level *ab initio* study on the conformational structure and vibrational spectra of HO_2NO_2 . Our calculated structure is also in good agreement with their results.

B. Potential energy surface

The electronic energies of IS1 and IS2 calculated by CCSD(T)/aug-cc-pVDZ method are -355.29078 and -355.29079 Hartree, respectively. Unless otherwise specified, the relative energies are used in the following discussions by taking the electronic energy of IS1 as zero for reference. IS1 and IS2 are a pair of mirror image isomers and they have the same relative energies, thus we only focus on the reaction channels for IS1 in the following discussion. We have tried our best to find a transition state for the O3–N4 bond breaking in IS1 to produce HO_2 and NO_2 but we failed. Thus we have to scan the PES along the O3–N4 bond at CCSD(T)/aug-cc-

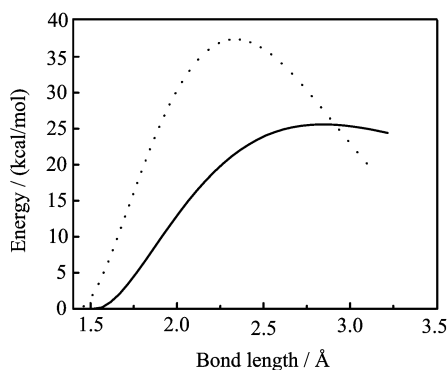


FIG. 2 The potential energy surface along the O3–N4 bond (solid line) and O2–O3 bond (dotted line) for peroxynitric acid scanned by CCSD(T)/aug-cc-pVDZ method.

pVDZ level. The results are shown in Fig.2. When the O3–N4 bond is stretched to about 2.82 Å, the energy of IS1 reaches the maximum value of 25.6 kcal/mol, which is similar to a transition state (loose transition state). As far as we know, this loose transition state has not been reported in the literatures. The energy barrier we calculated agrees very well with previous experimental and theoretical results. Experimentally, Gierczak *et al.* [5] recommended that for the reaction of $\text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$, the standard reaction enthalpy, $\Delta_r H_{298\text{K}}^\circ = 24.0 \pm 0.5$ kcal/mol. And theoretically, Szakács *et al.* [6] reported that for the reaction, $\Delta_r H_{298\text{K}}^\circ = 23.4 \pm 0.7$ kcal/mol. Zabel [3] also studied the rate constant experimentally, and obtained the low and high pressure activation energies $E_{a,0}$ and $E_{a,\infty}$, which were 19.9 and 21.6 kcal/mol, respectively. Our calculated result is a little larger than their data. And the O3–N4 bond dissociation energy (BDE) we calculated is 23.9 kcal/mol, in good agreement with Zabel's result. At B3LYP/6-311++G(3df,3pd) level, Staikova *et al.* [4] calculated the reaction energy for HO_2NO_2 dissociation to HO_2 and NO_2 , which was 21.2 kcal/mol (2.7 kcal/mol lower than our O–N BDE). Because of the low energy, this is the primary path for HO_2NO_2 dissociation.

The other feasible decomposition channel for HO_2NO_2 is the direct O2–O3 bond cleavage to yield HO and NO_3 , and we have not found the transition state, either. Thus we also scan the potential energy surface along the O2–O3 bond in IS1. From Fig.2, the energy barrier of IS1 reaches the maximum value of 37.4 kcal/mol when the O2–O3 bond is elongated to about 2.35 Å. And this loose transition state has also not been reported before. Due to the high energy barrier, it is difficult for this path to occur.

IV. CONCLUSION

We have studied the lowest energy structures of peroxynitric acid by B3LYP/6-311++G(2d,2p) method.

The calculations show that there is a pair of mirror image isomers, the geometric parameters are in good agreement with previous studies. At CCSD(T)/aug-cc-pVDZ level, we scanned the PES along the O–N and O–O bonds in peroxynitric acid for the first time, respectively. On the O–N PES, the loose transition state has the energy 25.6 kcal/mol, and agrees very well with the literatures, where the O3–N4 bond is stretched to 2.82 Å. Furthermore, on the O–O PES, the loose transition state with a 2.35 Å O2–O3 bond, has the energy 37.4 kcal/mol. Due to its lower energy barrier, peroxynitric acid dissociation into HO_2 and NO_2 is the primary path.

V. ACKNOWLEDGMENTS

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