Theoretical Study on Mechanism of Reaction of OH with HO$_2$NO$_2$

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The reaction of HO$_2$NO$_2$ (peroxynitric acid, PNA) with OH was studied by the hybrid density functional B3LYP and CBS-QB3 methods. Based on the calculated potential energy surface, five reaction channels, H$_2$O+NO$_2$+O$_2$, HOOH+NO$_3$, NO$_2$+HO$_2$H, HO$_2$+HONO$_2$ and HO$_2$+HOOONO, were examined in detail. The major reaction channel is PNA+OH→M1→TS1→H$_2$O+NO$_2$+O$_2$. Taking a pre-equilibrium approximation and using the CBS-QB3 energies, the theoretical rate constant of this channel was calculated as 1.13×10$^{-12}$ cm$^3$/(molecule s) at 300 K, in agreement with the experimental result. Comparison between reactions of HOOONO+OH and HONO$_2$+OH was carried out. For HOR+OH reactions, the total rate constants increase from R=NO$_2$ to R=O=NO$_2$, which is consistent with experimental measurements.

Key words: Reaction, Peroxynitric acid, *ab initio* calculation, Rate constant

I. INTRODUCTION

HO$_2$NO$_2$ (peroxynitric acid, PNA) is formed in the atmosphere by the association reaction of HO$_2$ with NO$_2$. As early as 1977, Nike et al. verified that HO$_2$NO$_2$ was a molecule, and not a simple complex, by using IR spectrum [1]. After that there have been considerable efforts in the study of the formation and loss processes of PNA, including the preparation, decomposition photochemistry and pulse radiolysis.

It has been confirmed that the PNA molecule plays an important role in the Earth’s upper troposphere and lower stratosphere (UTLS) as a reservoir for both HO$_2$ and NO$_2$ radicals, depending on the products of these two processes.

The concentration of reactive impurities. In addition, the unambiguous mechanism of reaction (3) is still not clear.

In this work, a high level of theory is employed to study the mechanism of the reaction of OH+PNA. The information on the potential energy surface (PES) is directly obtained from *ab initio* calculations. Such investigation can provide useful information for chemical-dynamic analysis.

II. COMPUTATIONAL METHODS

All of the electronic structure calculations in our present study were carried out with the Gaussian 03 program [14]. The geometries of the reactants, products, intermediates, and transition states of the reaction HO$_2$NO$_2$+OH were fully optimized by using the hybrid density functional B3LYP method with the CBSB7(6-311G(2d,d,p)) basis set. Vibrational frequencies were calculated at the same level to determine the nature and zero-point energy (ZPE) corrections of the stationary points. Each saddle point was verified to connect the proper reactants and products by performing an in-
trinsic reaction coordinate (IRC [15]) calculation. The single point energy calculations for all species were performed at the multilevel techniques based on additive energy corrections of CBS-QB3 [16]. In this work, additional calculations were carried out in some cases using G3B3 method to confirm the energies obtained by the CBS-QB3 method. Unless otherwise specified, the CBS-QB3 single-point energies are used in the following discussions.

III. RESULTS AND DISCUSSION

The optimized geometries of stationary points are shown in Fig.1. The overall energy profile based on the CBS-QB3 method is depicted in Fig.2. The vibrational frequencies including available experimental data for PNA are summarized in Table I and the scaled harmonic vibrational frequencies of the main stationary points are listed in Table II.

A. Structure and vibrational frequencies of PNA

Some theoretical studies have been performed to investigate pernitric acid [17-20]. Chen and Hamilton showed that a minimum structure calculated with the B3LYP method was similar to that calculated with both MP2 and QCISD methods using similar size basis sets [18]. Aloisio et al. obtained the geometry of PNA using the B3LYP method [20], which is in line with the structure calculated by Chen and Hamilton. Meanwhile, Jitaru et al. achieved three rotational isomers for PNA at different levels of theory and their calculations also indicated that the three isomers have the same energy at the G2MP2 level of theory [19]. More recently, Matthews and Sinha studied the structure and vibrational spectra of HO$_2$NO$_2$ using a high-level ab initio method [21]. They revealed that there was a significant basis set dependence in the predicted ab initio structure for PNA, and the calculations with the smaller basis set may not provide an accurate representation of the experimental geometry for PNA. Based on these results, the basis set 6-311++G(2df,2p) was employed to calculate the geometry of PNA in this work. The singlet geometries of PNA obtained in these calculations with two different basis sets are given in Fig.1. The global minimum structure is in good agreement with that calculated by Saxon et al. [17] and Jitaru et al. [19], having no symmetry and the plane of the HO$_2$ group roughly perpendicular to the plane of the NO$_2$ group. The dihedral angles of HOON are 87.3° and 88.0° with the CBSB7 and 6-311++G(2df,2p) basis sets, respectively, which are in line with 85.9° at the CCSD(T)/aug-cc-pVTZ level [21].

Frequencies and IR intensities calculated for PNA in the present work are given in Table I along with the observed values [22-24]. From Table I it can be seen that all of the MP2 calculations of Chen et al. [18] and Jitaru et al. [19] and the CCSD(T) calculations of Matthews et al. [21] overestimated the higher frequencies. The unscaled frequencies here based on B3LYP calculations are in line with their results. In contrast, in Table II, it is very clear that the scaled frequencies (scale factor is 0.96) of PNA in these calculations are in good agreement with the available experimental values. At the B3LYP/CBSB7 level the rotational constants $A=12.039$, $B=4.613$, $C=3.375$ GHz were also generated; they are in good agreement with the experimental values ($A=11.994$, $B=4.665$, $C=3.397$ GHz) [24]. The results indicate the method used in this work is appropriate.

B. Channels for HO$_2$NO$_2$+OH reactions

In these calculations there are five channels to produce five products, H$_2$O+NO$_2$+O$_2$ (P1), HOOH+NO$_3$ (P2), NO$_2$+HO$_2$ (P3), HO$_2$+HONO$_2$ (P4), and HO$_2$+HOONO (P5), and four intermediate complexes, HOHONO$_2$ (M1), (HO)$_2$NO (M2), HOON(O)$_2$OH (M3a and M3b).

\[
\text{PNA} + \text{OH} \rightarrow \text{M1} \rightarrow \text{TS1} \rightarrow \text{P1} \quad (4)
\]

A pre-reaction hydrogen-bonded complex M1 (O$_2$NOOH) is formed due to the dipole-dipole interaction between the oxygen atom of the OH radical and the hydrogen atom of PNA, as illustrated in Fig.1. The forming HO···H bond is 1.894 Å in M1, which is in the range of hydrogen bond length 1.7-2.3 Å, while the O5–H6 bond is elongated to 0.982 Å. The dihedral angle of NOOH is reduced to 81.3°, and the formation of HOH angle is 92.5°. The relative energies calculated at the CBS-QB3 and G3B3 levels of theory for M1 are $-19.2$ and $-18.8$ kJ/mol, respectively.

M1 can decompose to P1 via a transition state TS1. This is an N$_2$O+O$_4$ and O$_5$–H$_6$ scission and O–H$_6$ formation process. The breaking N$_2$O–O$_4$ and O$_5$–H$_6$ bonds in TS1 are elongated to 1.546 and 1.022 Å, respectively. Meanwhile, the forming O–H$_6$ bond is shortened to 1.468 Å. At the same time the angle of HOH6 increases to 110.3°, tending to form an H$_2$O molecule. Energetically, TS1 is located at 1.2 kJ/mol above the reactants, while the relative energy calculated at the G3B3 level for TS1 is 14.6 kJ/mol. Considering the different levels of theory, such differences are reasonable. The relative energy of product P1 is $-193.9$ kJ/mol.

\[
\text{PNA} + \text{OH} \rightarrow \text{TS2} \rightarrow \text{P2} \quad (5)
\]

The oxygen atom of OH radical can attack one of the oxygen atoms of PNA to form the product P2. With the approaching of O7 and O5 and the stretching of O4–O5, the transition state TS2 is reached. In TS2 the forming O5–O7 bond is shortened to 1.793 Å while the
FIG. 1 Optimized structures of various species involved in the reaction of HO$_2$NO$_2$ with OH at the B3LYP/6-311G(2d, d, p) level, the values in parentheses were calculated using the 6-311++G(2df,2p) basis set. Bond distances are in Å and angles are in (°).

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FIG. 2 The overall profile of the potential energy surface for the reaction of OH with HO$_2$NO$_2$, calculated at the CBS-QB3 level.

### TABLE I Vibrational frequencies (cm$^{-1}$) and assignments for HO$_2$NO$_2$

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<td>3791</td>
<td>52</td>
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<tr>
<td>1960</td>
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<td>1951</td>
<td>254</td>
<td>1822</td>
<td>1821</td>
<td>1728</td>
<td>[22] O1NO3 asym str</td>
</tr>
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<td>1445</td>
<td>1410</td>
<td>54</td>
<td>1431</td>
<td>1426</td>
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<td>1324</td>
<td>200</td>
<td>1365</td>
<td>1355</td>
<td>1304</td>
<td>[22] O1NO3 sym str</td>
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<td>1215</td>
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<td>973</td>
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<td>995</td>
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<td>786</td>
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<td>822</td>
<td>807</td>
<td>803</td>
<td>[22] O1NO3 sciss</td>
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<td>753</td>
<td>721</td>
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<td>738</td>
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<td>821</td>
<td>669</td>
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<td>37</td>
<td>657</td>
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<td>654</td>
<td>[23] O1NO4 bend</td>
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<td>457</td>
<td>410</td>
<td>89</td>
<td>454</td>
<td>450</td>
<td>483</td>
<td>[23] NO4 str</td>
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<td>378</td>
<td>356</td>
<td>61</td>
<td>377</td>
<td>370</td>
<td>340</td>
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<td>302</td>
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<td>19</td>
<td>304</td>
<td>299</td>
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*Unscaled frequencies calculated in this work, the values in parentheses were calculated using the 6-311++G(2df,2p) basis set.

Breaking O4−O5 bond is elongated to 1.674 Å. From Fig.1 we can also see that the N−O4 bond is shortened to 1.391 Å. The relative energies of TS2 and P2 are 67.7 and −49.3 kJ/mol, respectively, while the calculated energy of TS2 at the G3B3 level is 76.5 kJ/mol.

\[
PNA + OH \rightarrow TS3 \rightarrow P3
\]  \hspace{1cm} (6)

Besides the O5 atom, the O4 atom of the PNA molecule can also be attacked by the O atom of the OH radical. This is a direct reaction process via a transition state TS3 with a barrier of 68.6 kJ/mol. This indicates that TS3 and TS2 have nearly the same energy at the CBS-QB3 level. From Fig.1 we can see that the forming O4−O7 bond in TS3 is shortened to 1.904 Å while the breaking N2−O4 bond is elongated to 1.979 Å. The relative energy of P3 is −41.8 kJ/mol.

Since the P3 product has not been detected in past experimental research, this reaction channel was also calculated using the G3B3 method. The relative energy of TS3 was determined to be 83.2 kJ/mol. From above results we can see that at the G3B3 level the relative energy of TS3 is only 6.7 kJ/mol higher than that of
TABLE II  Vibrational frequencies of species for the PNA+OH reaction at the B3LYP/CBSB7 level of theory

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequencies/cm⁻¹</th>
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<tbody>
<tr>
<td>PNA</td>
<td>143, 292, 362, 436, 630, 708, 789, 955, 1310, 1374, 1749, 3571</td>
</tr>
<tr>
<td>OH</td>
<td>3557</td>
</tr>
<tr>
<td>M1</td>
<td>64, 107, 147, 207, 226, 317, 351, 448, 607, 674, 735, 793, 960, 1301, 1440, 1719, 3733, 3512</td>
</tr>
<tr>
<td>M2</td>
<td>56, 96, 195, 234, 303, 341, 403, 457, 561, 676, 729, 847, 942, 1337, 1355, 1483, 3553, 3581</td>
</tr>
<tr>
<td>M3a</td>
<td>111, 225, 248, 357, 385, 450, 475, 539, 635, 656, 829, 847, 939, 1102, 1372, 1386, 3562, 3577</td>
</tr>
<tr>
<td>M3b</td>
<td>93, 248, 340, 361, 403, 521, 533, 622, 688, 808, 832, 923, 1140, 1346, 1381, 3501, 3558</td>
</tr>
<tr>
<td>TS1</td>
<td>361f, 56, 76, 184, 216, 304, 381, 446, 598, 632, 715, 778, 991, 1298, 1383, 1754, 3588</td>
</tr>
<tr>
<td>TS2</td>
<td>689f, 76, 120, 238, 241, 354, 396, 592, 609, 703, 733, 854, 893, 1207, 1283, 1639, 3371, 3613</td>
</tr>
<tr>
<td>TS3</td>
<td>423f, 48, 103, 127, 187, 202, 234, 351, 373, 512, 737, 752, 951, 1326, 1383, 1743, 3542, 3608</td>
</tr>
<tr>
<td>TS4</td>
<td>567f, 70, 119, 237, 267, 280, 371, 421, 589, 620, 755, 876, 965, 1158, 1362, 1434, 3572, 3602</td>
</tr>
<tr>
<td>TS5</td>
<td>147f, 44, 145, 225, 263, 298, 374, 399, 532, 634, 736, 858, 946, 1341, 1358, 1507, 3570, 3575</td>
</tr>
<tr>
<td>TS6</td>
<td>289f, 104, 261, 301, 372, 383, 438, 463, 550, 634, 672, 901, 946, 1201, 1384, 1422, 3564, 3594</td>
</tr>
<tr>
<td>TS7</td>
<td>263f, 114, 244, 370, 383, 455, 473, 540, 626, 678, 831, 849, 936, 1126, 1332, 1377, 3563, 3589</td>
</tr>
<tr>
<td>TS8</td>
<td>1264f, 87, 229, 250, 338, 355, 446, 485, 567, 583, 804, 826, 957, 1073, 1320, 1362, 3531, 3555</td>
</tr>
<tr>
<td>TS9</td>
<td>1338f, 104, 199, 245, 276, 368, 384, 556, 613, 682, 784, 835, 942, 1131, 1388, 1602, 2063, 3555</td>
</tr>
</tbody>
</table>

TS2, and there is only a 0.8 kJ/mol difference between TS2 and TS3 at the CBS-QB3 level. Thus we conclude that the channel of the formation of the P3 product is also feasible. Based on these results, future experimental studies are strongly desired to confirm this channel.

It is very interesting that P4 can be formed through two different pathways. One is a direct reaction via a four-membered ring transition state TS9 with a barrier of 242.4 kJ/mol. The other is a consecutive reaction process. Firstly, the O atom of the OH radical is added to the N atom of the PNA molecule via a transition state TS6 with the formation of the complex M3a. The corresponding barrier is 130.4 kJ/mol. Then M3a isomerizes to M3b via an H–ON rotational transition state TS7. Finally, M3b decomposes to the final product P4 via an N2–O4 breaking transition state TS8. The relative energies of M3a, TS7, M3b, TS8, and P4 are 99.5, 113.3, 96.6, 120.0, and ~104.1 kJ/mol, respectively. Owing to the higher barrier for the two processes, they do not play an important role in the overall reaction.

\[
PNA + OH \rightarrow TS4 \rightarrow M2 \rightarrow TS5 \rightarrow P5
\]  

(7)

here is another channel that can produce the HO₂ radical. The PNA and OH radical may approach each other through the O atom of the OH radical and the O1 atom of the PNA molecule to form a complex M2 via a transition state TS4. With the gradual approach of the O atom of the OH radical to the O1 atom of the PNA molecule and the stretching of the N2–O1 bond, the TS4 structure occurs. In TS4 the forming O7–O1 bond is 1.586 Å and it is shortened to 1.434 Å in M2, while the N2–O1 bond is elongated to 1.313 Å in TS4 and it is only stretched by 0.155 Å in M2. As shown in Fig.2, M2 can further decompose to HO₂ and HOONO via an N–O breaking transition state TS5 with a small barrier of 4.6 kJ/mol. The breaking N2–O4 bond in TS5 is elongated to 1.617 Å, while the O4–O5 bond is only slightly shortened by 0.006 Å. The calculated relative energies of TS4, M2, TS5, and P5 are 114.1, 112.0, 116.6, and 23.4 kJ/mol, respectively. This pathway has been confirmed by IRC calculations. Note that the barrier is so high that this process does not easily occur at room temperature.

The schematic description of the PES of the reaction is shown in Fig.2. Indeed, P1 is a preferable product in view of thermodynamics because it has the lowest energy among the five products. Since it has the lowest barrier, taking kinetics into account, P1 is still the dominant product. As a result, we believe that \( \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 \) is the main product for the title reaction and this is in good agreement with the experimental observations [4,11-13]. In view of kinetics, we can see that the channel of formation for product P3 is also a feasible pathway, which is not in line with the conclusions by Jiménez et al. [4]. Jiménez et al. studied the reaction of PNA + OH by producing OH via pulsed laser photolysis (PLP) and detecting OH via laser-induced fluorescence (LIF). They also reported the first experimental determination of the product branching ratios for reaction (3). They concluded that the branching ratios for the production of P2 and P4 at 298 K were <5% and <10%, respectively, and \( \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 \) (P1) were the dominant products. The product P3 was not reported in their work.

In addition, the enthalpy changes \( \Delta H^\circ_{298} \) between the \( \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 \) reactions are strongly desired to confirm this channel.
reactants and products for the reaction of PNA+OH at CBS-QB3 level are also calculated. The $\Delta H_{298}$ of the P1 pathway is $-188.9$ kJ/mol at the CBS-QB3 level, which is in good agreement with the JPL 02-25 value of $-191.4$ kJ/mol [25]. For the P2 and P4 channels, the $\Delta H_{298}$ between the reactants and the products are $-49.3$ and $-106.2$ kJ/mol, respectively, which are also in line with the JPL values of $-46.4$ and $-104.1$ kJ/mol [25], respectively. However, for the channels of products P3 and P5 there are no comparable experimental values. The calculated $\Delta H_{298}$ values in this work are $-43.1$ and $23.8$ kJ/mol, respectively. As a result, in view of thermodynamics the channels of products P3 and P5 do not play important roles in the overall reaction. Moreover, the theoretical rate constant of product P1 pathway was calculated using the CBS-QB3 energies. In 2001, Alvarez-Idaboy et al. studied the reactions of OH with CH$_2$O and CH$_3$CH$_3$O [26]. They proposed that the reaction occurs according to the following two-step mechanism

Step1: \[ \text{RHC} = O + \text{OH} \leftrightarrow [\text{RHC} = O \cdots \text{HO} \cdot ] \] (8)
Step2: \[ [\text{RHC} = O \cdots \text{HO} \cdot ] \rightarrow \text{RC} = O \cdot + \text{H}_2\text{O} \] (9)

They believed the reaction involved a fast pre-equilibrium between the reactants and the prereactive complex followed by an internal rearrangement leading to the elimination of a water molecule. If $k_f$ and $k_r$ are the rate constants for the forward and reverse reactions of the first step, respectively, and $k_b$ is the rate constant for the second step, then the rate constant for the overall reaction can be written as

\[
k = \frac{k_f k_b}{k_r} = \frac{A_f A_b}{A_r} \exp \left( -\frac{E_f + E_b - E_r}{RT} \right)
\] (10)

In this reaction, the energy difference between the barrier $E_r$ and $E_b$ is only $0.12$ kJ/mol. However, the entropy change in the reverse reaction of the first step reaction is larger than that in the formation of the products of the second step reaction. Thus, one can expect $k_r$ to be considerably larger than $k_b$ [27]. Based on this assumption, they obtained a reliable result [26]. For the reverse process of M1 formation in OH+PNA reactions, the variation transition state theory (VTST) was used in the current work to obtain the value of $k_r$, which is truly higher than $k_b$. As a result, for this complex consecutive process: PNA+OH$\rightarrow$M1$\rightarrow$P1, the same method was used as Alvarez-Idaboy et al. used in Ref.[26] to calculate the rate constant. The calculated rate constant is $1.13 \times 10^{-12}$ cm$^3$/(molecule s) at 300 K. The experimental result was $3.42 \times 10^{-12}$ cm$^3$/(molecule s) [4].

C. Comparison with the HNO$_3$+OH reaction

The dominant loss of HO$_2$ in the lower stratosphere is due to the reactions of the hydroxyl radical with peroxynitric acid (HO$_2$NO$_2$) and with nitric acids (HONO$_2$ or HNO$_3$) [28]. Thus it is very meaningful to compare the PES feature of the reaction of HO$_2$NO$_2$+OH with that of the analogous reaction HONO$_2$+OH.

In 2000, Xia et al. studied the mechanism of the OH+HONO$_2$ reaction by ab initio molecular orbital calculations at the G2M(cc3) level of theory [29]. They reported four different reaction channels including four complexes and four transition states. The possible reaction pathways are summarized as

\[
\begin{align}
\text{OH} + \text{HONO}_2 & \rightarrow \text{LM1} \rightarrow \text{TS1} \rightarrow \text{H}_2\text{O} + \text{NO}_3 \\
& \rightarrow \text{LM2} \rightarrow \text{TS2} \rightarrow \text{H}_2\text{O} + \text{NO}_3 \\
& \rightarrow \text{LM3a} \rightarrow \text{TS3} \rightarrow \text{LM3b} \\
& \rightarrow \text{TS4} \rightarrow \text{H}_2\text{O}_2 + \text{NO}_2
\end{align}
\] (11)

By comparing the theoretical results, we find that both reactions involve the same initial association process, that is, the oxygen-to-hydrogen process, HOR+OH$\rightarrow$HO-HOR (R=ONO$_2$, NO$_2$), to form a molecular complex through hydrogen bonding with no barrier. Xia et al. reported two different structures of HO-HONO$_2$, and they both dissociate to the products H$_2$O and NO$_3$. In their work the calculated hydrogen bond lengths ranged from 1.683 Å to 1.817 Å, which are slightly shorter than that of the HO-HOONO$_2$ system (1.894 Å). From the PES of these two different systems, we can see that the pathway of the complex HO-HOR (R=ONO$_2$, NO$_2$) decomposition to the final products is the main reaction channel in their reaction systems. Both of them have the lowest energy barriers. In the HO+HONO$_2$ system, the barrier height is 27.6 kJ/mol at the G2M(cc3) level.

In order to study the relation between the structure and properties for the analogous reactions and find a proper method to study the kinetic behavior for the reaction of HO$_2$NO$_2$+OH, the OH+HONO$_2$→LM2→TS2→H$_2$O+NO$_3$ pathway was also calculated using the CBS-QB3 method. The results indicate that the optimized geometries of LM2 and TS2 at the B3LYP/CBSB7 level of theory are in good agreement with those reported by Xia et al. [29]. The relative energies of LM2 and TS2 were calculated as $-19.6$ and $6.7$ kJ/mol at the CBS-QB3 level, respectively. These values are also consistent with those obtained by Xia et al. [29]. The dissociation energy of LM2 is about 26.3 kJ/mol, which is a little higher than that of the HO+HOONO$_2$ system (20.5 kJ/mol). This difference was probably caused by NO$_3$ radicals with higher electronegativity than that of NO$_2$ radicals, which strongly attracts the electrons located on the OH radical. Thus, theoretically, the hydrogen atom in the PNA molecule has more positive charges than that in the HONO$_2$ molecule.

For these two reactions, it is obvious that they both have the reaction channel that forms the HOOH molecule. Meanwhile, as discussed above, the NO$_3$ radicals have higher electronegativity than that of the NO$_2$ radicals, which leads to the O–O bond rupture of the

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The HOONO molecule being easier than the N–O bond cleavage of the HONO2 molecule. At the CBS-QB3 level the O–O bond energy of PNA is 158.4 kJ/mol, while the N–O(H) bond energy of HONO2 is 201.9 kJ/mol. Furthermore, based on the PES, the energy barriers are 67.7 kJ/mol for the O–O bond rupture in the PNA+OH reaction and 102.0 kJ/mol for the N–O bond fission in the OH+HONO2 reaction, respectively. These theoretical predictions are in agreement with the experimental results. The experimental rate constants of HOR with OH radical (298 K) are (6.2±0.4)×10^{-12} cm^3/(molecule s) for R=NO ([12] and (1.4±0.2)×10^{-13} cm^3/(molecule s) for R=NO2 ([12], respectively.

It should be pointed out that in the reaction system of OH+PNA, there also is an N–O bond cleavage reaction pathway with a barrier of 68.6 kJ/mol, which is competitive with the O–O fission reaction channel. Moreover, three adduct complexes M2, M3a, and M3b also formed for the reaction of OH+PNA, while only two hydrogen bonding complexes LM3a and LM3b were obtained in the OH+HONO2 system.

IV. CONCLUSION

The hybrid density functional B3LYP method, G3B3 method and CBS-QB3 method were used to investigate the PES for the reaction of HO2NO2(PNA) with OH. Four intermediate complexes, nine transition states and five product channels, H2O+NO2+O2 (P1), HOOH+NO3 (P2), NO2+HO2H (P3), HO2+HONO2 (P4) and HO2+HOOH (P5), were examined in detail. Based on the PES, the major reaction channel is PNA+OH→M1→TS1→P1, via a very lower barrier height. Based on the pre-equilibrium approximation between the reactants and the prereactive complex, the theoretical rate constant of product P1 pathway is calculated by using the CBS-QB3 energies. The calculated rate constant is 1.13×10^{-12} cm^3/(molecule s) at 300 K, which is in agreement with the experimental result (3.42×10^{-12} cm^3/(molecule s)). A comparison of the HONO2+OH reaction with the analogous reaction of HONO2+OH was carried out. For the HOR+OH reactions, the total rate constants increase from R=NO2 to R=ONO2, which is consistent with the experimental measurements.

V. ACKNOWLEDGMENT

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