Theoretical investigation of the reaction mechanism of atomic oxygen radical anion with pyridine

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1. Introduction

The atomic oxygen radical anion (O−) is one of the most active anions [1,2], and can react rapidly with most molecules. The ion–molecule reactions involving the O− anion have stimulated a variety of studies in many fields, such as ionospheric chemistry, combustion chemistry, catalytic chemistry, negative ion chemical ionization mass spectrometry (NICI-MS) [3–7]. More importantly, such ion–molecule reactions have been widely used to synthesize various anions of the classical intermediates in organic chemistry [1,8]. For instance, o-benzylene radical anion (o-C6H4−) is produced in the reaction of O− with benzene [9,10], and vinylidene anion (CH2=CH−) is formed in the reaction of O− and ethylene [11]. Therefore, it is necessary to investigate these reactions extensively for atmospheric chemistry, radiation chemistry, organic and biologic chemistry. Moreover, these reactions will give insights into syntheses of organic intermediate anions and mechanisms of liquid-phase chemical reactions.

Pyridine (C5H5N) is one of the most important six-membered heterocyclic compounds, which can be seen as resulting from a reaction of nitrogen atom replacing one CH group in benzene molecule. Thus the reaction mechanism of O− with pyridine should be similar to that of O− with benzene [12,13], and several interesting anions are expected to be produced in this reaction, like C5H4NO− and C5H4N2−. However, as far as we know, only a few experimental studies of the reaction between O− with pyridine have been done, and the related thermochemical data are unavailable. The possible reaction pathways of O− with pyridine in thermodynamics are listed as follows:

\[
\begin{align*}
O^- + C_5H_5N & \rightarrow C_5H_4NO^- + H, \text{ oxide anion formation} \\
& \rightarrow C_5H_4N^- + H_2O, \text{ H₂-abstraction} \\
& \rightarrow C_5H_5N + OH, \text{ H-abstraction} \\
& \rightarrow C_5H_4N^- + OH., \text{ H^−-abstraction} 
\end{align*}
\]

Guo and Grabowski [14] applied the flowing afterglow (FA) technique to study the reaction of O− with pyridine, and only two anionic products, C5H4N− and C5H4NO− were detected. The corresponding branching ratios were: C5H4N− + H2O 46%, C5H4NO− + H 54%. Anionic products of the reaction of O− with perdeuterated pyridine (C5D5N) were measured as well, and similar branching ratios were reported: C5D5N− + D2O 38%, and C5D4NO− + D 62%. Bruins et al. [15] studied the title reaction in a double-focusing mass spectrometer, and found that the C5H4NO− anion was the dominant ionic product, along with a prominent peak of C5H4N− and a low intensity peak corresponding to C5H4N− in mass spectra. It was a pity that no branching ratios for these anionic products were measured.

The previous experiments can only offer a little information about anionic product channels, and a clear reaction mechanism is very difficult to be deduced from the detected anionic products. More significantly, some secondary reactions of the anionic products are probably involved in the previous experiments, which could cause contamination of the measured anions, as suggested...
in Ref. [1], e.g. the OH− can react rapidly with the pyridine. Therefore, high-level theoretical calculations are necessary to clarify reaction mechanisms, since the theoretical calculations are believed to be more powerful to describe details of reaction processes.

To our knowledge, no such theoretical study has been performed for this title reaction yet. In this work, density-function theory (DFT) is applied to explore the reaction potential energy surfaces (PESs) of O− with pyridine. The molecular structures of all species are optimized, and the possible thermodynamic reaction pathways are examined in detail. Based on our calculations, the formation mechanisms for those anions detected in the previous experiments will be presented, and the favorable product channels will be identified. Additionally, a lot of useful information will be provided for further study of the reactions of O− with heterocyclic compounds, through comparing mechanisms of the title reaction and the reaction of O− + C6H6.

2. Computational methods

All calculations were carried out using the Gaussian 03 program package [16]. The DFT-B3LYP method [17,18] and G3MP2B3 high-level energy calculations [19] were applied to study the reaction of O− with pyridine, as the previous studies [20–23] showed that these methods performed well to deal with open-shell reaction systems with one negative charge. Geometries of reactants, products, intermediates (denoted as IMs) and transition states (denoted as TSs) were optimized at the B3LYP level with the 6-31+G(d,p) basis set, and the harmonic vibrational frequencies and zero point energies (ZPEs) [scaled by 0.96 [19]] were calculated at the same level. In order to reveal the influence of different basis sets on the molecular geometries, the 6-311++G(d,p) basis set was also used to re-optimize the key species. Mass-weighted intrinsic reaction coordinate (IRC) calculations [24,25] were performed for the transition states to identify the corresponding reactants and products. Meanwhile, Mulliken charge population analysis [26] was employed to reveal charge transfers during the reaction process. To obtain high-precision energy, the G3MP2B3 method was performed to calculate the single-point energies, relative energies of all key species and reaction enthalpies of the corresponding production channels. In the present G3MP2B3 calculations, the projected MP2 (MPM2) [27–29] energies were used to replace the UMP2 energies to avoid the spin contamination effect. In addition, the standard 6-31G(d) basis set in the B3LYP optimization step of G3MP2B3 method was substituted by the 6-31+G(d,p) basis set to involve the possible diffuse electron effect on the title reaction system. In order to insure the reliability of our G3MP2B3 energies, the BPW91 [30], B3P86 [31] and ROMP2 [32,33] methods with the large basis set aug-cc-pVTZ [34] were employed as well to calculate the barrier heights of the oxide anion formation channel (1) and the H2−-abstraction channel (2).

3. Results and discussions

The B3LYP optimized geometry of pyridine is shown in Fig. 1, where Mulliken charge populations of each H atom is presented as well. Due to the π-bond conjugate in pyridine, the heterocycle is partially electronegative, whereas the hydrogen atoms are partially electropositive. As a result of the charge induction effect, the electropositive H atom is strongly attracted by O− to form initial intermediate when O− approaches pyridine. Since there are three different types of hydrogen atoms in a pyridine molecule: one γ-H, two β-H and two α-H atoms, three corresponding initial reaction intermediates are expected to form. On the basis of this assumption, three different reaction PESs of O− with pyridine are studied separately using the B3LYP method. In present calculations, there are no obvious differences in the optimized geometries with the 6-31+G(d,p) and 6-311++G(d,p) basis sets. In the following sections, the B3LYP/6-31+G(d,p) geometries and the G3MP2B3 energies are used unless otherwise noted.

3.1. Oxide anion formation channel (1)

For the cases of O− attacking the γ-H or β-H of pyridine, an initial intermediate is located, respectively, on the entrance PES. The optimized geometries of these two intermediates are presented in Fig. 1 as well, where IM1 corresponds to that of O− attacking the γ-H, and IM2 is related to β-H. However, when O− approaches α-H of pyridine, no stable initial intermediate has been located on the entrance PES at the B3LYP level because of the strong charge repulsion between the lone pair of electrons of the nitrogen atom and the O− anion. But to our surprise, two transition states (TS11 and TS9) of isomerization from IM2 have been found successfully, which correspond, respectively, to the processes of O− approaching α-H and α-C. That means, all expected reaction processes and final production channels related to α-H can process through an isomerization from IM2. Additionally, the overall reaction mechanisms related to the γ-, β- and α-H atoms of pyridine are very similar, and thus we will mainly describe the case of O− attacking the γ-H in the following sections.

3.1.1. The case of O− attacking the γ-H of pyridine

When O− attacks the γ-H of pyridine at the initial reaction stage, IM1 (with C2v symmetry) will be formed. As shown in Fig. 1, the active C–H bond length in IM1 is elongated a bit to 1.108 Å and the distance between γ-H atom and O− is 1.665 Å, which is slightly shorter than a normal hydrogen bond length. Since IM1 has an energy of

![Fig. 1.](image-url)
72.2 kJ mol\(^{-1}\) lower than the initial reactants, it can easily further decompose or isomerize to various final products. The B3LYP optimized geometries of those key stationary points on the reaction PES of channel (1) are shown in Fig. 2, where the imaginary vibration modes of transition states are also presented. The G3MP2B3 energies, relative energies and reaction enthalpies of these species are listed in Table 1.

The overall reaction process to produce the oxide anion in the case of O\(^{-}\) attacking the \(\gamma\)-H can be represented as the following scheme.

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**Fig. 2.** The B3LYP optimized geometries of the key stationary points on the reaction PES of channel (1), where the upper and lower parameters are obtained with 6-31+G(d,p) and 6-311++G(d,p), respectively. Bond lengths are in Angstrom, and bond angles are in degree.
O\(^-\) + C\(_5\)H\(_4\)N \rightarrow \text{IM1} \begin{align*}
\text{T5} & \quad \text{T3}^2
\gamma\text{-C}_5\text{H}_4\text{NO}^- + \text{H} \\
\text{T5}^2 & \quad \text{IM4} \rightarrow \text{IM5} \\
\gamma\text{-C}_5\text{H}_4\text{NO}^- + \text{H}
\end{align*}

Obviously, the oxide anion formation products, $\gamma\text{-C}_5\text{H}_4\text{NO}^- + \text{H}$, can be produced from IM1 through two possible pathways. The more favorable pathway can be described as an isomerization-decomposition process. IM1 firstly isomerizes to IM3 via a transition state TS1. In this process, O\(^-\) approaches the active C atom from out of ring plane, the $\gamma$-H atom connected to the heterocycle is pushed out of plane and the single C–O bond is formed gradually. TS1 has a barrier height of 30.9 kJ mol\(^{-1}\) compared with IM1, but is still lower than the initial reactants in energy. In IM3, the distance between the C and O atoms is rapidly shortened from 2.115 Å in TS1 to 1.540 Å and the C–O distance is shortened to a typical double bond, and the O–H distance length has increased to 1.858 Å. As a typical product-like intermediate $\gamma\text{-C}_5\text{H}_4\text{NO}^- + \text{H}$, IM3 can finally decompose to products, $\gamma\text{-C}_5\text{H}_4\text{NO}^-$ and H.

For the two aforementioned reaction pathways to produce $\gamma\text{-C}_5\text{H}_4\text{NO}^- + \text{H}$, the energies of the two rate-controlling barriers, TS1 and TS3, are both lower than that of the initial reactants. Thus the oxide formation channel is favorable to happen, and the overall exothermic energy is 198.2 kJ mol\(^{-1}\). The first pathway, O\(^-\) + C\(_5\)H\(_4\)N \rightarrow IM1 \rightarrow IM3 \rightarrow $\gamma\text{-C}_5\text{H}_4\text{NO}^- + \text{H}$, should be dominant owing to its lower rate-controlling step barrier TS1.

### 3.1.2. The case of O\(^-\) attacking the $\beta$- and $\alpha$-H of pyridine

When O\(^-\) attacks the $\beta$- or $\alpha$-H of pyridine, a unique initial ion–dipole intermediate IM2 will be formed with C\(_5\) symmetry on the entrance PES. As mentioned above, two transition states (TS11 and TS9) have been found to correspond, respectively, to the subsequent processes of O\(^-\) approaching $\alpha$- and $\beta$-C, and thus the production channels (1–4) related to $\alpha$- position of pyridine will follow. As shown in Fig. 2, the imaginary vibration movement of TS11 actually corresponds to the $\alpha$- abstraction process, while the imaginary vibration mode of TS9 corresponds to the approach of O\(^-\) towards $\beta$-C atom and the $\alpha$-H rocking out of the heterocycle plane. In other words, TS11 and TS9 look like the initial transition states of the H-abstraction and oxide anion formation.

### Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>$\nu$ (cm(^{-1}))^a</th>
<th>ZPE (hartree)^b</th>
<th>$E_{\text{G}(\text{MP2}B3)}$ (hartree)</th>
<th>$\Delta E$ (kJ mol(^{-1}))</th>
<th>$\Delta H_{\text{298}}$ (kJ mol(^{-1}))</th>
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<td>C(_5)H(_4)N + O(^-)</td>
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<td>–196.1</td>
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<td>$\beta$-C(_5)H(_4)NO(^-) + H</td>
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<td>–169.6</td>
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<tr>
<td>$\alpha$-C(_5)H(_4)NO(^-) + H</td>
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<td>IM1</td>
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<td>–72.2</td>
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<td>IM2</td>
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<td>–82.4</td>
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<td>IM4</td>
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<td>IM5</td>
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<td>–322.99853</td>
<td>–201.8</td>
<td>–200.0</td>
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<td>–322.95527</td>
<td>–193.2</td>
<td>–191.3</td>
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<tr>
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<td>205(^t)</td>
<td>0.08389</td>
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<td>TS2</td>
<td>980(^t)</td>
<td>0.07815</td>
<td>–322.97736</td>
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<td>TS3</td>
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<td>–322.93228</td>
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<td>979(^t)</td>
<td>0.07866</td>
<td>–322.99806</td>
<td>–320.9</td>
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<td>TS6</td>
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<td>–322.97103</td>
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<td>TS7</td>
<td>1049(^t)</td>
<td>0.07775</td>
<td>–322.92928</td>
<td>–320.9</td>
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<tr>
<td>TS8</td>
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<td>0.07812</td>
<td>–322.98934</td>
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<td>TS9</td>
<td>392(^t)</td>
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<td>–322.92830</td>
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<tr>
<td>TS10</td>
<td>958(^t)</td>
<td>0.07778</td>
<td>–322.97356</td>
<td>–320.9</td>
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<tr>
<td>TS11</td>
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<td>0.07720</td>
<td>–322.93414</td>
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<td>TS12</td>
<td>842(^t)</td>
<td>0.07738</td>
<td>–322.99335</td>
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\(^a\) Calculated at the B3LYP/6-31+G(d,p) level.  
\(^b\) ZPEs are calculated with the vibrational frequencies scaled by 0.96 [19].
channels, respectively. Very interestingly, our reverse IRC calculations for TS11 and TS9 point to the same unexpected intermediate IM2, which is indeed an entrance intermediate complex formed by O/C0 attacking β-H. That means, the lone pair electrons of the nitrogen atom effectively hinder O/C0 from approaching the α-H atom to form a stable initial intermediate, and all subsequent reaction processes related with the α-H or α-C atoms of pyridine are originated from IM2 in fact. The forward IRC calculations for TS11 and TS9 point to IM10 and IM9, respectively, in both of which the active carbon atom is the β-C atom. Thus we still identify the subsequent reaction processes as the reaction pathways induced by O/C0 attacking α-H of pyridine, in order to be distinguished from the aforementioned reaction mechanism of O/C0 attacking β-H. As an example, the relative energy diagram for the static reaction pathway involving TS11 on the entrance PES is shown in Fig. S1 of Supplementary materials.

The subsequent oxide anion formation channels can be accomplished through the isomerization and decomposition of IM2, as shown in the following schemes.

\[
\text{O}^- + \text{C}_5\text{H}_5\text{N} \rightarrow \text{IM2} \xrightarrow{\text{TS5}} \text{IM6} \xrightarrow{\text{TS6}} \beta-\text{C}_5\text{H}_4\text{NO}^- + \text{H} \xrightarrow{\text{TS7}} \text{IM7} \xrightarrow{\text{TS8}} \text{IM8} \rightarrow \beta-\text{C}_5\text{H}_4\text{NO}^- + \text{H}
\]
The scheme (6) and (7) are related to the cases of O⁻ attacks the β- and α-H, respectively. The optimized geometries of the key species involved in these schemes are shown in Fig. 2 as well. The G3MP2B3 energies, relative energies and reaction enthalpies of the species are also summarized in Table 1.

As the overall reaction mechanism is similar to that of O⁻ attacking the γ-H, we just give brief descriptions of these product channels here. In scheme (6), the overall reaction process to produce β-C₅H₄N⁺⁺ anion is still exothermic by 171.8 kJ mol⁻¹ and all barriers involved are lower than the initial reactants in energy. The rate-controlling barriers for these two pathways are TS5 and TS7, whose heights are 46.8 and 62.5 kJ mol⁻¹, respectively. Due to a lower rate-controlling barrier, the pathway O⁻ + C₅H₅N → IM2 → IM6 → β-C₅H₄N⁺⁺ + H, is more favorable. The scheme (7) is very similar to the scheme (6). Both IM10 and IM9 are formed through exothermic reaction processes and can easily overcome the subsequent isomerization and dissociation barriers. The overall reaction process is exothermic by 189.7 kJ mol⁻¹. In the two pathways to produce α-C₅H₄N⁺⁺ anion, the rate-controlling barriers are TS11 and TS9, and the barrier heights are 49.7 and 65.0 kJ mol⁻¹, respectively. Therefore, the latter pathway, O⁻ + C₅H₅N → IM2 → IM10 → IM11 → α-C₅H₄N⁺⁺ + H, is more favorable.

3.2. H₂⁺-abstraction channel (2)

As previous studies have shown [1], the H₂⁺-abstraction process is another important reaction channel in the reactions of O⁻ with molecules containing hydrogen atoms. In the title reaction, the H₂O molecule can be produced from IM1 or IM2 via the following multi-steps schemes:

\[
\begin{align*}
\text{O}^- + \text{C}_5\text{H}_5\text{N} & \rightarrow \text{IM1} \rightarrow \text{IM4} \rightarrow \text{IM12} \rightarrow \beta, \gamma-\text{C}_5\text{H}_4\text{N}^+ + \text{H}_2\text{O} \quad (8) \\
\text{O}^- + \text{C}_5\text{H}_5\text{N} & \rightarrow \text{IM2} \rightarrow \text{IM13} \rightarrow \beta, \gamma-\text{C}_5\text{H}_4\text{N}^+ + \text{H}_2\text{O} \quad (9) \\
\text{O}^- + \text{C}_5\text{H}_5\text{N} & \rightarrow \text{IM2} \rightarrow \text{IM10} \rightarrow \alpha, \beta-\text{C}_5\text{H}_4\text{N}^- + \text{H}_2\text{O} \quad (10)
\end{align*}
\]

The schemes (8-10) correspond to the reaction cases of O⁻-approaching the γ-, β- and α-H atoms of pyridine. The B3LYP optimized geometries of these key stationary points on the reaction PES of channel (2) are shown in Fig. 3, where the imaginary vibration modes of transition states are also presented. The G3MP2B3 energies, relative energies and reaction enthalpies of the species are listed in Table 2.

In the overall reaction processes, the first isomerization steps from IM1 to IM4, IM2 to IM7 and IM2 to IM10, are the rate-determining steps for the H₂⁺-abstraction channel (2), respectively. In these isomerization processes, the OH group leaves from the heterocycle and approaches the neighboring H atom gradually. A new ion–dipole intermediate, C₅H₅N⁺⁻H₂O, is formed finally. Although the barrier energies involved is much higher than that of the entrance intermediates, IM1 or IM2, the overall H₂⁺-abstraction reaction is still energetically allowed. As shown in Table 2, the exothermic energies are 81.4 kJ mol⁻¹ for producing β,γ-C₅H₄N⁺⁺ + H₂O, and 46.8 kJ mol⁻¹ for producing α,β-C₅H₄N⁺⁺ + H₂O.

In order to compare all production pathways and identify the dominant channel, the schematic diagrams of the G3MP2B3 relative energies of various species on the reaction PES are shown in Fig. 4, in which Fig. 4a, b and c present the reaction mechanism of O⁻-attacking γ-, β- and α-H atom of pyridine, respectively.

As indicated in Fig. 4, the H₂⁺-abstraction channel (2) and oxide anion formation channel (1) can come from the same intermediate, but the subsequent barrier height of channel (2) is much higher than that of channel (1). Therefore, the H₂⁺-abstraction channel (2) is relatively less important than the oxide anion formation channel (1).

3.3. H-abstraction channel (3) and H⁺-abstraction channel (4)

The H-abstraction channel (3) and H⁺-abstraction channel (4) need an O⁻ insertion process to subsequently proceed. As mentioned above, three energetic intermediates are formed via the typical atom-insertion process, e.g. IM4 for γ-position reaction, IM7 for β- and IM10 for α- position. These intermediates can decompose directly by breaking the C–O bond, and two possible decomposition products are obtained: one is C₅H₄N⁺ + OH⁻ (H-abstraction channel (3)), and the other is C₅H₃N⁻ + OH⁺ (H⁺-abstraction channel (4)). The corresponding G3MP2B3 energies, relative energies and reaction enthalpies for these two channels are listed in Table 3, and the B3LYP optimized geometries of C₅H₄N and C₅H₃N⁻ in-

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**Table 2**

Total energies, relative energies and ZPEs of key species at 0 K, and reaction enthalpies at 298 K, for the H₂⁺-abstraction channel (2).

<table>
<thead>
<tr>
<th>Species</th>
<th>vᵣ (cm⁻¹)</th>
<th>ZPE (hartree)</th>
<th>E_G3MP2B3 (hartree)</th>
<th>ΔE (kJ mol⁻¹)</th>
<th>ΔH₂98 (kJ mol⁻¹)</th>
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<tr>
<td>C₅H₅N + O⁻</td>
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<td>-322.92168</td>
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<td>0.0</td>
<td>0.0</td>
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<td>β,γ-C₅H₄N⁺ + H₂O</td>
<td>0.08518</td>
<td>-322.92168</td>
<td>0.0</td>
<td>-81.4</td>
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<td>α,β-C₅H₃N⁻ + H₂O</td>
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<td>62.5</td>
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<td>IM4</td>
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<td>255.5</td>
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a Calculated at the B3LYP/6-31+G(d,p) level.

b ZPEs are calculated with the vibrational frequencies scaled by 0.96 [19].
Fig. 4. Schematic diagram of the G3MP2B3 relative energies of various species on the reaction PES. (a) $\text{O}^-$ attacks the $\gamma$-H atom of pyridine; (b) $\text{O}^-$ attacks the $\beta$-H; (c) $\text{O}^-$ attacks the $\alpha$-H atom.
Fortunately, both channels (3) and (4) are endothermic for all cases with each other and cannot be distinguished at the B3LYP level. The relative energy of the reaction system increases gradually as the C–O bond-breaking process. No barrier has been found and has been calculated with other coordinates optimized to monitor potential energy scan along the elongation of the C–O distance. Calculations have demonstrated that the oxide anion formation channel (1) and H2+-abstraction channel (2) are also favorable in thermodynamics while abstractions of the two channels are not distinct at all theoretical levels, as shown in Fig. 4. As shown in Fig. 4, the channels (1) and (2) proceed through the same intermediate, IM4 for γ–position reaction, IM7 for β– and IM10 for α–position. Thus the contradiction of branching ratios between present calculation and previous experiment [14] has been doubted as uncertainty of the G3MP2B3 method to calculate the related barrier heights in this open-shell reaction system. To confirm the error of G3MP2B3 level, some other popular quantum chemical computational theories have been chosen to calculate the barrier heights of the rate-controlling step of channel (2) and channel (1) in the three cases of the O– attacking γ-, β- and α-H of pyridine. Table 4 lists the calculated differences of the two rate-controlling barrier heights with G3MP2B3, B3LYP/6-31+G(d,p), B3LYP/aug-cc-pVTZ, B3PW91/aug-cc-pVTZ, B3P86/aug-cc-pVTZ and ROMP2/aug-cc-pVTZ methods, respectively. Obviously, the barrier height differences of the two channels are not distinct at all theoretical levels, and thus the present G3MP2B3 results should be reliable, indicating that more experimental investigations should be carried out to study the product branching ratios of this reaction system. It needs to be emphasized that the secondary reactions of those anionic products were probably involved in the previous experiment [14], which could cause contamination of the measured anions, as suggested in Ref. [1].

Additionally, in the mass spectra measured by Bruins et al. [15], a weak anion signal corresponding to C4H4N+ was detected besides the C4H4NO− and C4H3N− anions. According to our calculations, H+-abstraction channel (3) is difficult to occur, as well as H- abstraction channel (4). More importantly, the active energies for these two channels are very close in the case of O– attacking β- and γ-H of pyridine, even while more slight active energies are needed for H- abstraction than H- abstraction pathway in the case of O– attacking α-H. Therefore, the OH− anion should exist as well as the C4H4N− anion when the title reaction system has a high enough initial reaction energy, which obviously disagrees with the experimental results of Bruins et al. [15].

### 3.4. Comparison with experimental results

Although the barrier heights and reaction enthalpies of each product channel for the title reaction are slightly different in the three cases of the O– attacking γ-, β- and α-H of pyridine, reaction mechanisms are very similar as shown in Fig. 4. The present calculations have demonstrated that the oxide anion formation channel (1) is most dominant among the four reaction channels. The H2+-abstraction channel (2) is also favorable in thermodynamics while the H-abstraction channel (3) and H+-abstraction channel (4) are both inaccessible at room temperature. These conclusions agree qualitatively with the experimental results of Guo and Grabowski [14], in which only the anion products of channel (1) and channel (2) were obtained. However, the two anionic products they obtained were almost in equal quantities, which disagrees with our conclusion that oxide anion formation channel (1) is much more favorable than H2+-abstraction channel (2) due to its lower barrier height of the rate-controlling step.
this disagreement is that a trace of OH anion exists inevitably in the preparation process of O source, and its secondary reactions with pyridine caused the quenching of OH itself and the formation of the C5H4N anions. Because the proton affinity (PA) of OH anion is 1633 kJ mol⁻¹ [37,38], which is even higher than that of the O anion (1601 kJ mol⁻¹ [39]), it is a highly active anion and can abstract a proton of pyridine to produce the C5H4N anion. The similar secondary reaction process has been confirmed to contribute to the branching ratios of anionic products in the O + C4H6 reaction [22].

3.5. Comparison with the reactions of O and O

As shown in Fig. 4, the overall reaction processes of the title reaction is analogical to that of O + C4H6 [13], and the two reaction systems have similar initial ion–dipole intermediates formed on the entrance PES. Only in the case of attacking α-H of pyridine, the lone pair electrons of the nitrogen atom effectively hinder O from approaching the α-H to form the expected initial ion–dipole intermediate. Interestingly, the subsequent reaction processes seem to undergo the expected way similar to those in the cases of the O attacking β- and γ-H, in which the active reaction position of heterocycle is still α-H or α-C atoms.

Since ethylene (C2H4) is the simplest alkene, the reaction mechanism between it with O is another important example for us to understand the ion–molecule interaction. As the extensive potential energy profile mapped in Ref. [22] shown, the initial stage of the O + C2H4 reaction is also similar, and an ion–dipole intermediate complex will be formed when O approaches ethylene. Among all anionic production channels, the CH2CHO oxide anion formation is the most dominant due to the lowest barrier. All static production pathways are very similar between the title reaction with O + C2H4. Very recently, we have also explored the potential dynamic reaction pathways of the O + C2H4 reaction [40], compared with the static reaction mechanism revealed by IRC calculations. Interestingly, the reaction presents a few different dynamic production pathways, especially when the initial kinetic energy of reactants is relatively high. For instance, the formation of OH + CH2=CH products can depart from the minimum energy path (MEP) and bypass the deep potential well of intermediate. However, the oxide formation and H2 abstraction pathways do not present any dynamic effects yet. That means, the dynamic effect would be obvious only in the direct H-atom abstraction process between O and organic molecule, including the title reaction of O + CH2=CHN. Since the H (or H+) abstraction in the O + CH2=CH-N reaction is much endothermic than the oxide anion formation (1) and H2 abstraction (2) channels, this kind of dynamic effect will not cause serious contamination of branching ratio of the anionic products.

4. Conclusions

G3MP2B3 method has been applied to investigate the reaction mechanism of atomic oxygen radical anion with pyridine. On the entrance reaction PES, an initial ion–dipole intermediate is located, respectively, when atomic oxygen radical anion attacks γ- and β-H atom of pyridine, but no similar intermediate has been found when O attacks α-H. The lone pair electrons of the nitrogen atom in the heterocycle effectively hinder O from approaching α-H to form the expected initial ion–dipole intermediate. Interestingly, two unexpected isomerizations involving movement of O from β-H to α-H or α-C can happen in this case, and thus the subsequent reaction for O attacking α-H can progress on its normal way. Four possible thermodynamic product channels are investigated systematically on the reaction PES. Geometries of all species are optimized at the B3LYP/6-31+G(d, p) level, and high precision G3MP2 energies and reaction enthalpies are obtained subsequently. Although there are certain differences among the overall reaction processes when O initially attacks γ-, β- and α-H atoms, reaction mechanisms are very similar as shown in Fig. 4. Compared with the H2 abstraction (2), H-abstraction (3) and H+ abstraction (4) channels, the oxide anion formation channel (1) is dominant for its lowest barrier height. The H2 abstraction channel (2) is also favorable in thermodynamics, while the H-abstraction channel (3) and H+ abstraction channel (4) are both inaccessible at room temperature. The present conclusions are consistent qualitatively with the previous experimental results [14].

Based on our calculations, the detected C6H4N anion in the experiment of Bruins et al. [15] should come from secondary reactions of the OH anions involved in the experiment. The secondary reaction between OH with pyridine would cause the quenching of the OH anion itself and produce the C6H4N anion, because the OH anion is a highly active anion and it is able to fast abstract a proton of pyridine.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2010.07.032.

References