Theoretical study on the ozonolysis of α-humulene in the atmosphere

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Abstract: α-Humulene is a major sesquiterpene which is produced by plants and can easily react with ozone in the atmosphere. The ozonolysis mechanism of α-humulene in the atmosphere was investigated by density functional theory and calculated rate constants using transition-state theory in this paper. In the ozonolysis of α-humulene, primary ozonides (POZ) are first formed after an addition reaction. Then, with the broken O-O bond, Criegee intermediates (CIs) are formed. The results discussed the subsequent reaction of CIs in detail, including the formation of secondary ozonide (SOZ) and the reaction of CIs with H₂O. For the formation of SOZ, the path of SOZ6 is the best path in all six paths, with a low energy barrier (3.80 kcal mol⁻¹) and high total rate constants (3.34×10⁸ s⁻¹) at 298 K and 1 atm. For the reaction of CIs with H₂O, the production of P6 is the best path in all six paths, with a low energy barrier (9.87 kcal mol⁻¹) and high total rate constants (9.58×10⁻¹¹ cm³ molecule⁻¹ s⁻¹) at normal temperature and pressure. This work provides reaction mechanisms of the ozonolysis of α-humulene and finds the reliable paths in the subsequent reactions.

1. Introduction

Biogenic volatile organic compounds (BVOCs), including isoprene (C₅H₈), monoterpenes (C₁₀H₁₆), sesquiterpenes (SQTs, C₁₅H₂₄) and oxygenated hydrocarbons, can play an important role in troposphere and are also primary biogeochemical sources of secondary organic aerosol (SOA) formation.[1] Because of their high molecular mass and high reactivity in gas phase, in terms of the SOA yields, SQTs is more efficient in SOA formation than monoterpenes.[2,3] Some studies reported that the source strengths of SQTs emitted into the atmosphere by plants was about 15 Tg per year and the quantities of SQTs emissions were about 18 million metric tons of carbon per year.[4,5]

α-Humulene, which contains three carbon-carbon double bonds, is one of the monocyclic SQTs, and is emitted from vegetation into atmosphere through diffusion.[6] Many kinds of plants such as pine trees, thale cress, marsh elders and tobacco are proven to emit α-humulene.[7-10] Due to the existence of carbon-carbon double bonds, α-humulene can react with NO₃, OH radicals, and O₃ molecules easily, leading to the formation of many different types of oxygenated compounds and SOA.[11,12] Jaoui et al investigated the photooxidation of α-humulene in the presence of NOₓ.[13] They identified some reaction products using mass spectroscopy and proposed the reaction mechanism of α-humulene with OH radicals. The ozonolysis of α-humulene has also been studied by many researchers. Beck et al performed a study of ozone and α-humulene in gas phase.[14] They used FTIR spectroscopy to calculate the reaction rate constant of ozone with α-humulene and found many types...
of products species. And they also confirmed the formation of secondary ozonides (SOZ), which is followed the Criegee mechanism.[15] Xiao et al used QM/MM method to calculate the reaction of α-humulene and ozone at air-water/acetonitile interfaces.[16] In their studies, important implications for the formation of SOA were provided and the Criegee reaction mechanism near the marine boundary also was found. Though the ozonolysis of α-humulene has been investigated by many researchers, there is no theoretical calculation on the ozonolysis reaction and the subsequent reaction of α-humulene in gas phase.

In this paper, we investigated the reaction mechanisms of α-humulene with ozone using quantum chemical calculations. For studying the ozonolysis reaction more detail, we also calculated the reaction mechanism of CIs with H₂O and the formation of SOZ. In order to investigate which reaction path is the best, we also calculated total rate constants of subsequent reactions.

2. Computational methods

2.1. Mechanism computations
In this paper, all quantum chemistry calculations were performed by the Gaussian-09 suite of programs.[17,18] The M06-2X functional at the 6-31+g(d, p) basis set was used to optimize the geometries of reactants, pre-reactive complexes, transition states (TS) and products.[19] In order to confirm if the local minimum and the TS have zero and one imaginary frequency, the vibrational frequencies were calculated at the same level of theory. Meanwhile, the intrinsic reaction coordinate (IRC) calculations were used to prove whether the TS connected with the specific reactants and products.[20-22] The single point energies were carried out using the M06-2X functional with a standard 6-311++g(3df, 3dp) basis set. The geometries were drawn by the CYLview software package and the GaussView software.[23]

2.2. Kinetics computations
Kinetics analysis was calculated by using the KiSThelP program based on the transition-state theory (TST) with Winger tunneling correction. All rate constants were calculated on the basis of optimized geometric structure parameters and thermodynamic data.[24,25]
3. Results and discussion

3.1. The formation of POZ and CI

Figure 1 shows the optimized structure of α-humulene. As shown in Figure 1, there are three carbon-carbon double bonds in α-humulene, C\textsubscript{1}=C\textsubscript{2}, C\textsubscript{5}=C\textsubscript{6} and C\textsubscript{11}=C\textsubscript{12}. Due to the position of the three double bonds, the reactions of α-humulene and ozone have three possible reaction pathways. When ozone approaches α-humulene, three different types of pre-reactive complexes are formed by van der Waals interaction. Considering the potential energy barriers of the three pathways (path A, B and C) are only 0.94 kcal mol\textsuperscript{-1}, 4.13 kcal mol\textsuperscript{-1} and 0.98 kcal mol\textsuperscript{-1}, respectively, it can be inferred that α-humulene is easy to be transformed to the primary ozonides (POZ). The three types of POZ are formed with the potential energy release of 71.59 kcal mol\textsuperscript{-1}, 67.59 kcal mol\textsuperscript{-1}, 70.79 kcal mol\textsuperscript{-1}, respectively. The O-O bond and the C-C bond in the five-numbered ring are broken with exothermic process. As shown in Figure 2, each POZ can produce two Criegee intermediates (CIs). All potential energy barriers of six transform processes exceed 20 kcal mol\textsuperscript{-1}, and the formation of CI\textsubscript{1} is the best favorable because it has the lowest value of potential energy barrier (22.18 kcal mol\textsuperscript{-1}). It also can be found that these transform processes are exothermic.

Figure 2. Reaction pathways for the POZ and CIs formation and the potential energy changes (kcal mol\textsuperscript{-1}).

According to the analysis above, the formation reactions of three POZ are highly exothermic and have low potential energy barriers. Therefore, the ozonolysis of α-humulene is very easy to happen. By comparing the potential energy barriers of the reaction of three POZ formations, their differences are not obvious. Although the potential energy barrier of POZ\textsubscript{2} formation process is little higher than that of POZ\textsubscript{1} and POZ\textsubscript{3}, the value is still only 4.13 kcal mol\textsuperscript{-1}. By comparing the potential energy barriers of six CIs formation processes, the formation path of CI\textsubscript{2} is the most favorable and the reaction at CI\textsubscript{3} is the most difficult, but the differences are very close.
3.2. The formation of SOZ
Criegee intermediates (CIs) can react with many kinds of substances, such as NO₃, OH radicals and H₂O molecules in the atmosphere and can also reform a five-numbered ring (SOZ). Figure 3 shows the potential energy profile and optimized geometries of the six types of SOZ. As shown in Figure 2, there are two C=O double bonds and one O-O bond in each CI. First, the two C=O double bonds are broken in the process of the reaction. Then, the carbon atom of the C=O double bond on the Criegee free radical side connects with the oxygen atom on the carbonyl side, and the carbon atom of the C=O double bond on the carbonyl side connects with the oxygen atom of the O-O bond on the Criegee free radical side, rearranged a five-numbered ring. The comparison of potential energy changes of six pathways is also shown in Figure 3. The formations of six types of SOZ are all highly exothermic processes. Meanwhile, in Figure 3, it can be clearly found that the formation of SOZ6 has the lowest potential energy barrier (3.80 kcal mol⁻¹). Compared with other products, the potential energy barriers for other paths are significantly higher than SOZ6. The potential energy barriers of SOZ3 and SOZ4 are 6.41 kcal mol⁻¹ and 6.53 kcal mol⁻¹, respectively, and other potential energy barriers are much higher than them. It proves that the formation of SOZ6 is easier than other five types of SOZ. Finally, SOZ6 is formed with releasing the energy of 45.18 kcal mol⁻¹. For SOZ6, the distances between two oxygen atoms and two carbon atoms change from 2.63 Å to 1.42 Å and 1.76 Å to 1.41 Å, respectively. Although the comparison of energy changes in six pathways is performed, in order to determine the most favorable reaction path, we still calculated the rate constants, which will be discussed in detail later.
3.3. The reaction of CIs with H$_2$O

For SOA formation, the H$_2$O molecules have an important role. Thus, we calculated the reaction of CIs with H$_2$O. The reaction mechanism of CIs with H$_2$O is different from the formation of SOZ. In this reaction, an exothermic process occur first, producing pre-complexes CI…H$_2$O. Figure 4 shows the potential energy profile and optimized geometries of the pre-complexes. As shown in Figure 4, six types of CIs can react with H$_2$O to produce six types of pre-complexes. In the process of the reaction, at first, the pre-complexes CI…H$_2$O is formed by van der Waals interaction. The distance of H…C is significantly smaller than the distance of C…O. Then, the oxygen atom of H$_2$O molecules connects with the carbon atom of the C=O double bond in the Criegee free radical side. And one of the hydrogen atoms in H$_2$O molecules connects with the first oxygen atom in the Criegee free radical side. With the connection between oxygen atom and hydrogen atom, the C=O double bond is broken and C-O bond is formed. By analyze the potential energy barriers of the six paths, it is shown that the formations of P2, P5, and P6 are easier, which potential energy barriers are 7.76 kcal mol$^{-1}$, 9.44 kcal mol$^{-1}$ and 9.87 kcal mol$^{-1}$, respectively. In contrast, the potential energy barriers of other paths are all higher than 10.00 kcal mol$^{-1}$. Finally, with releasing the energy, the six types of products are formed.

Same as the analysis of SOZ formation, we also calculated the rate constants of the reaction of CIs with H$_2$O, which will be discussed in detail in the next part.

3.4. Rate calculation

After considering the energy of the reaction and optimizing the geometries, we also calculated the rate constants of the two reactions above. As discussed above, CIs has two subsequent reactions: one is the
formation of SOZ and the other is the reaction of CIs with H2O. Because the reaction occurs mainly in
the troposphere, we performed rate calculations in the range of 200 - 300 K. By using KiSThelP, we
calculated the formation rate constants of twelve products for the two type reactions. For the formation
reaction of SOZ, because of no pre-reactive complexes formed, the rate calculation formulas can be
expressed as equations (1) and (2).

\[
\text{Step 1: } CI \xrightarrow{k_1} SOZ \\
\text{The formula for the total rate constants of SOZ formation is shown as follows:}
\]

\[
k_{\text{total}} = k_1 \\
(2)
\]

For the reaction of CIs with H2O, the reaction mechanism consists of two parts, the formation
of pre-complexes and products. And the formulas of its mechanism can be characterized by equations (3)
and (4).

\[
\text{Step 1: } CI + H_2O \xrightarrow{k_1} CI \cdot \cdot \cdot H_2O \\
\text{Step 2: } CI \cdot \cdot \cdot H_2O \xrightarrow{k_{-1}} \text{Products} \\
\text{The formulas for the total rate constants of the reaction of CIs with H2O are shown as follows:}
\]

\[
k_{\text{total}} = K_{\text{eq}} \cdot k_2 \\
K_{\text{eq}} = \frac{k_1}{k_{-1}} \\
(5) \\
(6)
\]

Figure 5 shows the rate constants of the SOZ formation and Figure 6 shows the rate constants of
the reaction of CIs with H2O. As shown in Figure 5, in the 200 - 300 K range, the rate constants
of SOZ6 is about $10^7 - 10^9$ s$^{-1}$. The reaction rate constants of SOZ6 formation is significantly higher than
the other five products, which is about $10^3$ times of SOZ1, SOZ3 and SOZ4 formation and $10^8$ times
of SOZ2 and SOZ5 formation reaction. Combined with the analysis of the reaction energy barrier, the
reaction of SOZ6 formation is the fastest in all of the six paths. As shown in Figure 6, in the same
temperature range, the rate constants of P6 formation is about $10^{-11} - 10^{-8}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The rate
constants of P6 is the highest of all six paths, which is $10^4 - 10^6$ times of others. And the rate constants
of other paths are similar.

4. Conclusion
The path of SOZ6 formation is the best path for SOZ formation and the path of P6 formation is the best path for the reaction of CIs with H2O. In this work, the reaction mechanism and kinetics of the ozonolysis of α-humulene in the atmosphere have been calculated. The results show that the ozonolysis of α-humulene is carried under the Criegee mechanism. In the subsequent reaction, the potential energy barrier of SOZ6 formation is only 3.80 kcal mol\(^{-1}\), which is lower than other paths. The total rate constants of SOZ6 formation is \(3.34 \times 10^8\) s\(^{-1}\) at 298 K and 1 atm. For the reaction of CIs with H2O, the path of P6 is the most reliable path, with a low energy barrier (9.87 kcal mol\(^{-1}\)) and a high total rate constant (\(9.58 \times 10^{11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) at normal temperature and pressure. These results in this investigation can help scientists understand the reaction mechanisms of the ozonolysis of sesquiterpenes better and provide better supports for the research on α-humulene.

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