MS No.: egusphere-2023-2856

TITLE: *Rapid oxidation of phenolic compounds by O_3 and $HO^{\bullet}$: effects of air-water interface and mineral dust in tropospheric chemical processes*

Dear editor,

Thank you for your comments on our manuscript to enrich the content of this work. The first author of our manuscript, Yanru Huo, has recently started a postdoctoral position at McGill University. As a result, we would like to update the author's affiliation to include McGill University as the second affiliation. Due to the change in the type of our manuscript to a Research Article, we have made a small adjustment to the content. Specifically, the "Data Availability" section has been removed as all relevant data are now included in the supporting materials. We have tried our best to modify the manuscript according to your suggestions. Each question was answered in blue; every correction is in red, and the deleted texts are marked with a delete line number in this response. Besides, every correction is in red in the revised manuscript. The detailed response to each comment is shown as follows:

Reviewer #1:

Question 1: Please provide a better explanation for choosing phenol, 4-hydroxybenzaldehyde and vanillin. For example, are these species observed in the atmosphere, and are they major types of phenolic compounds in the atmosphere?

Author reply: The manuscript has been modified in Line 106, "Increasing the number of constituents on the aromatic ring would affect the reactivity and lead to complex compounds after reaction addition and/or open ring pathways. Phenol (Ph), 4-hydroxybenzaldehyde (4-

HBA), and vanillin (VL) are typical lignin pyrolysis products (Jiang et al., 2010; Kibet et al., 2012) ".

Question 3: please modify the manuscript to address this comment. Answering the question in just the "response to referees" is not sufficient.

Author reply: The manuscript has been modified:

Line 175 "After analyzing the stability of the wavefunction, the method we used is reliable".

Line 178 "The frequency correction factor (0.967) has been taken into account".

Reviewer #2:

Question 5: The authors state that "... the troposphere ranging between 9.85*10^11 molec cm^-3". Please indicate a lower limit. If you say a range, there needs to be an upper and lower limit.

Author reply: The ozone concentration has been updated in the manuscript in Line 304:

"O_3 is a major oxidant in the atmosphere, with high concentrations in the troposphere of 9.85 $\times 10^{11}$ molecules cm $^{-3}$ (Tomas et al., 2003; Pillar-Little et al., 2014) ".

Reviewer #3:

Question 13, 14, 19, 28, 41: Please modify the manuscript to address these comments/questions. Answering the questions in just the "response to referees" is not sufficient.

Question 13) l. 130-131: The manuscript should state how the random selection was executed in this work.

Author reply: The manuscript has been revised in line 139:

"Prior to the formal simulation, six Ph molecules were randomly selected position placed in a vacuum above the water box for 150 nanoseconds of NVT molecular dynamics simulations".

Question 14: l. 132: The manuscript should explain to the readers of ACP why such a short 150 ns period is relevant. The explanation should be followed by establishing the relevance of this period to what happens in the environment.

Author reply: It appears that there might be some confusion between the timescale used in molecular dynamics simulations and the real-world timescale of environmental processes. Molecular simulations, though conducted over short periods like 150 ns, are designed to capture essential molecular dynamics that occur on this time scale, such as bond formation, conformational changes, and interaction events.

These simulations provide detailed insight into microscopic mechanisms, which, although happening in a simulated timeframe, can offer valuable predictive power about long-term macroscopic processes. The results from such simulations can be extrapolated to understand how molecules behave under real-world environmental conditions. Thus, the 150 ns simulation period is highly informative for understanding key molecular interactions that are relevant on a larger environmental timescale.

Line 141: In order to make the experimental scientists understand that the time of the molecular simulation and the time when the reaction occurs are not one and the same concept, clarification was made in the manuscript. "The purpose of simulating 150 ns is to capture the fundamental molecular dynamics that occur on this time scale, such as bond formation, conformational changes, and interaction events".

Question 19: l. 159: What is the meaning of “benchmarking” here? Clarify the text.

Author reply: It has been modified in the manuscript. Line 172: "Calculated at the CCSD(T)/cc-pVDZ, CBS-QB3, B3LYP/6-311+G(d,p), MP2/6-311+G(d,p) and M06-2X/6-311+G(d,p) levels, Cao et al. (Cao et al., 2021) found that M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p) is reliable for PhCs at gas phase".

Question 28: l. 213: Why should the reader care about the return to the "bulk water"? Shouldn't be more important the return to "air"? The model approached the irrelevant problem and missed the relevant problem questioning its validity.

Author reply: This part of the response has been added to the manuscript in Line 289:

"Reactions inside the aqueous particle have also been a hot topic of interest in recent years (Tilgner et al., 2021; Mabato et al., 2023; Zhang et al., 2024; Rana et al., 2024) , so we also focused on the process by which phenolic compounds enter the interior of the droplet".

Question 41: l. 364: What do the authors mean by the "… TiO_2 clusters are the most favorable"?

Author reply: The manuscript has been revised in line 351:

"Among the three aromatic compounds, the $R_{RAF\text{-}HO}$• routes of VL on TiO_2 clusters are most likely to take place (**Fig. 4(n)**) ".

Question 35: should "physorption" be changed to "physisorption".

Author reply: In Line 269, "physorption" has been changed to "physisorption".

Question 42: I think the referee is indicating that you should not state that "aromatic compounds react with O_2". The mechanism is more complicated than a direct reaction, so your statement is not exactly accurate.

Author reply: The manuscript has been revised in line 406:

"For the purposes of this discussion, the primary atmospheric fate of the selected aromatics was considered to be their reactions with O_2 (typically mediated by reactive intermediates or catalytic processes) and O_3".