

We thank the reviewer for their thoughtful and constructive comments, and we have revised the manuscript accordingly. Listed below are our point-to-point responses (in blue) to the comments (in black) and changes of the manuscript (in red).

Responses to Reviewer 1:

Comments:

This study examines the evolution of chemical and optical properties of phenolic aqSOA generated via $\bullet\text{OH}$ - or $^3\text{C}^*$ oxidation during photoaging, as well as the effects of increased concentration of oxidants. The changes in the chemical composition and light absorption of aqSOA were tracked using HR-AMS and UV-Vis spectroscopy. The findings for the $^3\text{C}^*$ -aqSOA have been reported in a previous study by the same group (Jiang et al., 2021). Although this paper attempted to explain the differences between $^3\text{C}^*$ -aqSOA thoroughly and $\bullet\text{OH}$ -aqSOA, several statements appear unclear or not clearly supported by the results. The paper is well organized, but several points need clarification.

1. Could the authors give examples of products likely resistant to fragmentation?

In our previous studies on phenolic aqSOA formation from syringol, we have observed that certain dimeric products, such as $\text{C}_{15}\text{H}_{16}\text{O}_9$, proposed as 3',5,5'-Trimethoxy[1,1'-biphenyl]-2,2',3,4,4',6'-hexol, are more stable than other oligomeric and functionalized products, and can remain in large abundance after illumination equivalent to several days of atmospheric aging (Yu et al., 2016). We hypothesize that similar dimeric products of GA may also be more resistant to fragmentation. However, due to the lack of molecular-level characterization in this study, we are unable to identify which specific products are more resistant to fragmentation in GA aqSOA.

2. Were the 4 aliquots prepared for further aging also continuously stirred?

Yes, the solutions were continuously stirred during further aging. This information has now been added to Sec. 2.1. of the updated manuscript at line 114.

3. Section 3.2: why would $\bullet\text{OH}$ production from $^3\text{C}^*$ be more important during prolonged photoaging? is there any evidence for this?

H_2O_2 can be produced via the oxidation of phenols with $^3\text{DMB}^*$, in which a ketyl radical is formed and subsequently reacts with O_2 to produce $\text{HO}_2\bullet$ that undergoes self-reaction to generate H_2O_2 . Moreover, it has been found that the H_2O_2 concentration increases significantly with illumination time in the reactions of phenols with $^3\text{DMB}^*$ (Anastasio et al., 1997). Thus, it is possible to expect higher H_2O_2 and $\bullet\text{OH}$ concentrations during prolonged photoaging. We have included this reference in the updated manuscript. Furthermore, we have provided Scheme 1 to illustrate $\bullet\text{OH}$ production from the reaction of GA with $^3\text{C}^*$.

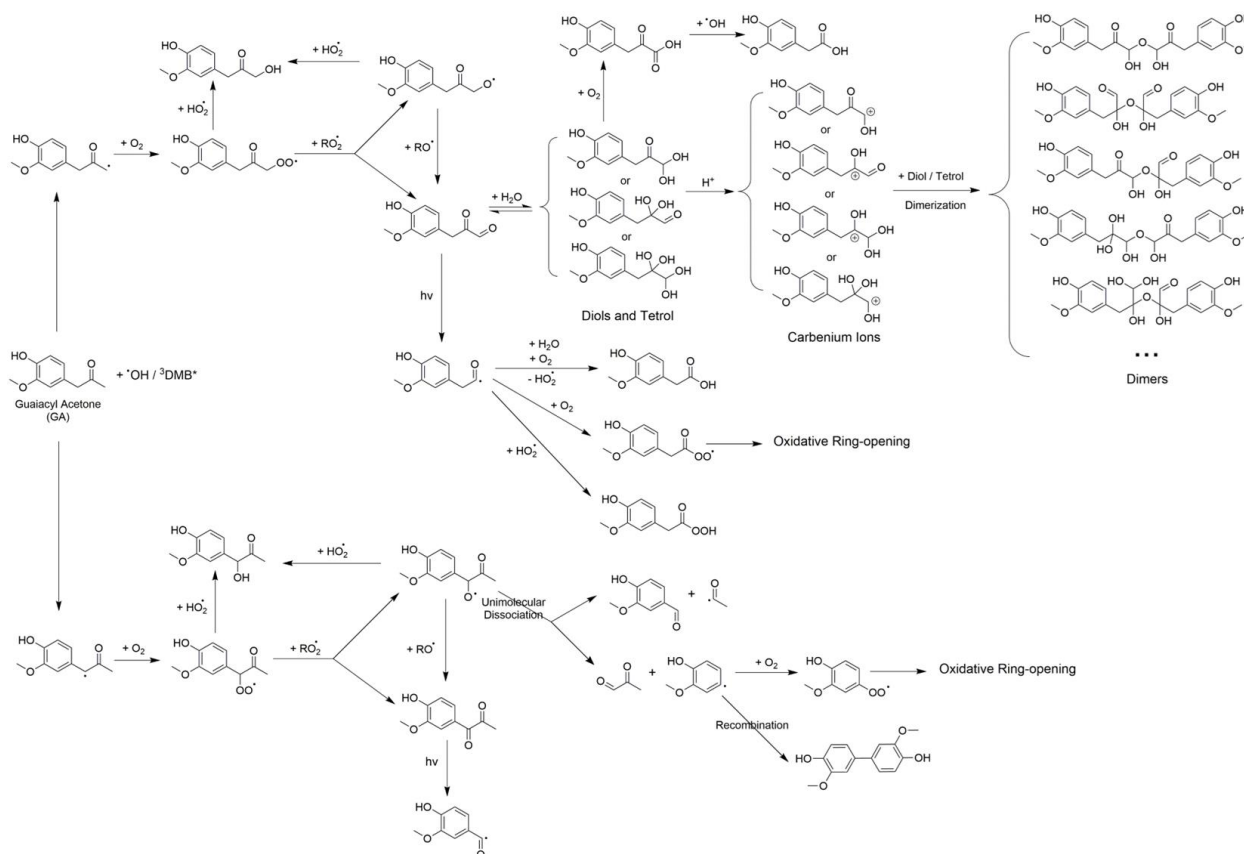
In Sec 3.1, we compared the aqSOA formation from the $\bullet\text{OH}$ and $^3\text{C}^*$ reactions of GA. When $\sim 95\%$ of GA reacted, the $\bullet\text{OH}$ -aqSOA showed a higher degree of oxidation and a more enhanced production of volatile compounds than the $^3\text{C}^*$ -aqSOA, as evidenced by the higher bulk O/C ratio and lower mass yield of the $\bullet\text{OH}$ -aqSOA (Figures 1d, 1f, 1k and 1m). This result suggests that oxidative ring-opening pathways are more promoted in the $\bullet\text{OH}$ reaction of GA, whereas oligomerization and functionalization are more pronounced in the $^3\text{C}^*$ reaction during the initial aqSOA formation period. However, the aqSOA's vulnerability to degradation depends on the light absorptivity and the quantum yield of photodegradation of the aqSOA. Therefore, the difference in photo-vulnerability of the two aqSOA types cannot be determined solely based on the initial aqSOA formation pathways. We have revised Sec 3.1 accordingly and the text has now been updated as follows.

Line 181: In addition, the results suggest that the photodegradation of $\bullet\text{OH}$ -aqSOA of GA has a higher tendency than $^3\text{C}^*$ -aqSOA to form volatile and semi-volatile compounds that evaporate from the condensed phase.

5. Section 3.2: Could the authors explain why acid formation is more pronounced in the aging of $^3\text{C}^*$ -aqSOA? In section 3.1, it was mentioned that $\bullet\text{OH}$ -aqSOA has a greater tendency to form volatile and semi-volatile compounds that evaporate from the condensed phase.

Our HR-AMS analysis revealed that the $^3\text{C}^*$ -aqSOA is less oxidized and has a higher oligomer content compared to the $\bullet\text{OH}$ -aqSOA. Since the formation of acids is mainly driven by ring-opening reactions of GA and its derivatives (as depicted in Schemes 1 and 2), this compositional difference suggests that $^3\text{C}^*$ -aqSOA contains a greater concentration of acid precursors, which could potentially explain the more pronounced acid formation observed during its aging.

To illustrate the reaction pathways of GA and the possible product formation, we have included Schemes 1 and 2 in the updated manuscript.



Scheme 2. Postulated reaction pathways triggered by the ketone functional group of GA.

6. Section 3.2: What are the differences between the highly oxidized products from $^3\text{C}^*$ and $\bullet\text{OH}$ oxidation? Those from $^3\text{C}^*$ are stated to be resistant to degradation, while those from $\bullet\text{OH}$ are mentioned to degrade over long aging times. Also, why are some of the highly oxidized products less reactive with $^3\text{C}^*$ than with $\bullet\text{OH}$, and that they can persist in the aqueous phase?

Our PMF results show that small, oxygen-containing ions are predominant in the 3rd-generation $^3\text{C}^*$ -aqSOA factor but are enriched in both 2nd- and 3rd-generation $\bullet\text{OH}$ -aqSOA. The 2nd-generation $\bullet\text{OH}$ -aqSOA factor decays faster and earlier than the 3rd-generation factor, suggesting that the $\bullet\text{OH}$ -aqSOA may comprise some highly oxidized products that belong to the 2nd-generation and are susceptible to degradation. However, the highly oxidized products in $^3\text{C}^*$ -aqSOA are primarily classified as 3rd-generation and are expected to be more resistant to degradation.

However, it should be noted that the interpretation of the PMF results presented above is just one possible explanation. In this study, we were not able to provide molecular information on the highly oxidized products generated from $^3\text{C}^*$ and $\bullet\text{OH}$ reactions, and thus a direct comparison between them is challenging. We will pursue a more detailed understanding of the composition and degradation pathways of these products in our future studies. To prevent misinterpretation, the text in the manuscript has been revised as follows.

Line 335: One possible reason for the observed difference is that $\bullet\text{OH}$ reaction tends to form highly oxidized products that degrade over long aging times, whereas the $^3\text{C}^*$ reaction can generate highly oxidized SOA products that are more resistant to degradation.

On the other hand, previous studies have shown that the reactivity of $^3\text{C}^*$ is sensitive to electron availability (Walling and Gibian, 1965), while $\bullet\text{OH}$ can react rapidly with a wide range of organic compounds in the condensed phase at diffusion-controlled rates (Herrmann et al., 2010). Therefore, it is possible that electron-poor products may exhibit insignificant reactivity towards $^3\text{C}^*$, but they can still undergo further oxidation by $\bullet\text{OH}$. This may also contribute to the degradation of highly oxidized products in the $\bullet\text{OH}$ -aqSOA over long aging times, whereas the highly oxidized products in $^3\text{C}^*$ -aqSOA are primarily classified as 3rd-generation and are expected to be more resistant to degradation. The text in the manuscript has been updated as follows for clarification.

Line 337: Another possible explanation for the observed difference in the evolution of $^3\text{C}^*$ -aqSOA and $\bullet\text{OH}$ -aqSOA is that the highly oxidized species in the aqSOA exhibit different reactivity with $^3\text{C}^*$ and $\bullet\text{OH}$ due to their electron availability (Walling and Gibian, 1965). In general, $^3\text{C}^*$ is known to be less reactive with electron-poor compounds, whereas $\bullet\text{OH}$ can rapidly react with a wide range of organic compounds in the aerosol at diffusion-controlled rates (Herrmann et al., 2010). As a result, electron-poor products may persist in $^3\text{C}^*$ -aqSOA, while $\bullet\text{OH}$ has the capability to further oxidize these products, eventually transforming them into volatile species.

7. Section 3.3: Why would the higher oxidation degree of $\bullet\text{OH}$ -aqSOA lead to the destruction of chromophores?

In this context, "oxidation" pertains specifically to the oxidative ring-opening reactions or bond breaking which destroy the conjugation in chromophores. To clarify, the text has been updated as follows in the manuscript.

Line 367: Nevertheless, the 2nd-generation $\bullet\text{OH}$ -aqSOA shows relatively lower MAC values ($\text{MAC}_{365\text{nm}} = 0.47 \text{ m}^2 \text{ g}^{-1}$) than the 2nd-generation $^3\text{C}^*$ -aqSOA ($\text{MAC}_{365\text{nm}} = 0.89 \text{ m}^2 \text{ g}^{-1}$). This difference could be attributed to the more pronounced oxidative ring-opening reactions that cause the destruction of conjugation in $\bullet\text{OH}$ -aqSOA, resulting in the breakdown of chromophores.

8. Section 3.4: Why would $\bullet\text{OH}$ be more reactive with non-phenolic organic compounds? For example, a study on the oxidation of green leaf volatiles (Richards-Henderson et al., 2015) comprising both non-phenolic and phenolic compounds did not show a general trend in the reactivity with $^3\text{C}^*$ and $\bullet\text{OH}$.

In Section 3.4, we aim to explain that $^3\text{DMB}^*$ is a more selective oxidant that prefers to react with electron-rich species such as phenols (Walling and Gibian, 1965), whereas $\bullet\text{OH}$ reacts fast with a wide range of organic compounds in the aqueous phase at nearly diffusion-controlled rates (Herrmann et al., 2010). Although GA reacts fast with both $^3\text{DMB}^*$ and $\bullet\text{OH}$, some electron-poor aqSOA products may be less reactive with $^3\text{DMB}^*$ than with $\bullet\text{OH}$. Previous studies on the oxidation of green leaf volatiles also suggest a higher selectivity of $^3\text{DMB}^*$ than $\bullet\text{OH}$. For example, the aqueous second-order rate constants for the oxidation of the green leaf volatiles by $^3\text{DMB}^*$ at pH 5 and 298 K are in the range of $0.13\text{--}15 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, with the most reactive cis-3-hexenyl acetate (HxAc) being 115 times more reactive than the least reactive 2-methyl-3-butene-2-ol

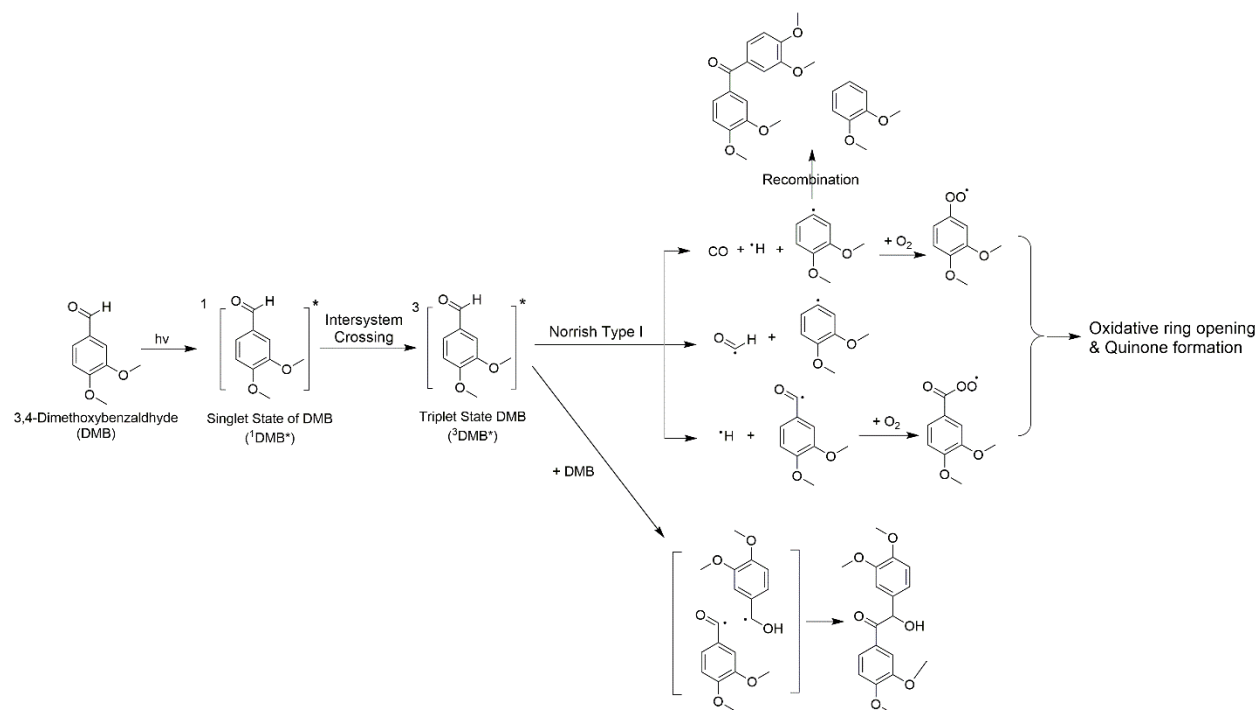
(MBO) (Richards-Henderson et al., 2015). However, under the same conditions, the aqueous second-order rate constants for these green leaf volatiles with $\bullet\text{OH}$ are in the range of $5.3\text{--}8.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, with the most reactive HxAc being only 1.6 times more reactive than the least reactive cis-3-hexen-1-ol (HxO) (Richards-Henderson et al., 2014).

To improve the clarity of our interpretation, the text in the manuscript has been updated as follows.

Line 401: This result may reflect the reactivity differences between GA and the aqSOA towards the oxidants, i.e., while both oxidants react quickly with GA, for the electron-poor aqSOA products, $^3\text{C}^*$ may be much less reactive whereas $\bullet\text{OH}$ can oxidize them rapidly.

9. Section 3.4: Could the authors give some examples of these unique low-volatility, light-absorbing products that cannot be generated via $\bullet\text{OH}$ oxidation?

In this context, we are talking about the products generated from the photodegradation of DMB. According to previous studies, the photo decay of benzaldehydes can lead to the formation of dimeric products and quinones that possess highly conjugated structures and can efficiently absorb UV-vis light (Theodoropoulou et al., 2020). Scheme S1 has been added to the supplementary materials to illustrate the potential product that may arise from the photodegradation of DMB.



Scheme S1. Postulated reaction pathways for the photodegradation of 3,4-dimethoxybenzaldehyde. The mechanisms are adapted from previous studies on benzaldehydes (Berger et al., 1973; Dubtsov et al., 2006; Shen and Fang, 2011; Theodoropoulou et al., 2020).

10. Section 3.4: What do the authors mean by $\bullet\text{OH}$ only accounts for a small fraction of the total oxidant amount in the $^3\text{C}^*$ -initiated reaction system?

In the $^3\text{C}^*$ -initiated experiment, the estimated concentration of $^3\text{C}^*$ produced by 5 μM DMB is approximately 10^{-13} M, while the estimated concentration of $\bullet\text{OH}$ produced by the addition of 100 μM H_2O_2 is approximately 10^{-14} M, which is 10 times lower than the $^3\text{C}^*$ concentration.

Minor comments and questions:

11. Intro: Is hydroxylation an example of functionalization?

Yes. Functionalization includes hydroxylation. The text in the manuscript has been updated as follows.

Line 44: The mass yields of phenolic aqSOA range from 50% to 140%, and the proposed formation pathways include oligomerization, functionalization (e.g., hydroxylation) and fragmentation (Arciva et al., 2022; Huang et al., 2018; Jiang et al., 2021; Ma et al., 2021; Smith et al., 2014, 2015, 2016; Sun et al., 2010; Yu et al., 2014, 2016).

12. Please provide more information on the HPLC method used to determine the concentration of GA and DMB.

The detection method for GA and DMB has been added to the manuscript in Sec 2.2.

Line 124: The concentrations of GA and 3,4-DMB were determined by a high-performance liquid chromatograph equipped with a diode array detector (HPLC-DAD, Agilent Technologies Inc.). A ZORBAX Eclipse XDB-C₁₈ column (150×4.6 mm, 5 μm) was used with a mobile phase consisting of a mixture of acetonitrile and water (20:80), and the flow rate was 0.7 mL min⁻¹. Both GA and DMB were detected at 280 nm, and their retention times were 8.349 and 15.396 min, respectively.

13. Please correct what [Org]_t and [GA]_t refer to.

Done.

14. There are other recently published articles regarding the formation of aqSOA by $^3\text{C}^*$ chemistry and the corresponding light absorption by reaction products (e.g., Li et al., 2022, <https://doi.org/10.5194/acp-22-7793-2022>; Mabato et al., 2023, <https://doi.org/10.5194/acp-23-2859-2023>)

Thanks for this comment. We have now added citations to these articles in the revised manuscript.

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