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Mar. 9, 2026

Dear Prof. Arthur Chan,

Revision for Manuscript egusphere-2025-4646

We thank you very much for giving us the opportunity to revise our manuscript. We sincerely appreciate your comments and suggestions on the manuscript entitled "**Mechanistic investigations of the formation of multifunctional products from the multi-generation ·OH oxidation of styrene**". We have carefully revised the manuscript according to your comments and suggestions. All revisions are highlighted in blue for clarity. The response letter is attached at the end of this cover letter.

We hope that the revised manuscript can meet the requirement of *Atmospheric Chemistry & Physics*. If there are any further modifications or revisions, please do not hesitate to contact us.

Looking forward to hearing from you as soon as possible.

Best regards,

Yu Huang

Comments of Editor

After going through reviewers' comments and reading through the manuscript myself, I believe that this manuscript needs major revisions before it can be considered for publication.

Response: We sincerely appreciate your comments and have carefully revised the manuscript. Following is our point-by-point response.

1. Line 25 and 66: styrene is not necessarily the 2nd most "efficient". SOA yields for PAHs can be higher than toluene and styrene. It is unclear what "efficient" means.

Response: Based on the Editor's suggestion, the relevant explanations have been added in the revised manuscript. Sun et al. investigated the characteristics, secondary organic aerosol formation potential (SOAP), and contributing factors of volatile organic compounds (VOCs) during haze episodes in Beijing from 18th October to 6th November 2013 (Sun et al., 2016). The SOAP of alkanes, alkenes and aromatics is determined using the fractional aerosol coefficient (FAC) method, which is expressed as Eq. (1):

$$FAC = [SOA]/[VOCs]_0 \quad (1)$$

where [SOA] and [VOCs] refer to the SOAP and initial mixing ratios of VOCs, respectively. SOAP of aromatics is 6.5 ± 6.4 ug m^{-3}, which is significantly greater than that of alkanes and alkenes (0.3 ± 0.2 and 1.1 ± 1.0 ug m^{-3}). Among these precursors, toluene is the predominant SOA-forming species, contributing more than 16% of the total SOA, followed by styrene (15%) and ethylbenzene (9.5%) (Sun et al., 2016). The 2nd-most "efficient" in the revised manuscript means that styrene has the second-largest SOAP during haze episodes in Beijing. Therefore, in the present study, styrene is selected as the model compound to investigate the formation mechanism of multifunctional products arising from multi-generation OH oxidation reactions.

In the laboratory chamber and flow tube experiments, the SOA yields of the photooxidation of aromatics are highly sensitive to the concentrations of NO_x (Ng et al., 2007). In general, the SOA yields under low-NO_x conditions are greater than those under high-NO_x conditions, which can be attributed to the reactions of peroxyl radicals with NO_x (Ng et al., 2007; Yu et al., 2024). For the photooxidation of toluene and styrene, the SOA yields under low-NO_x conditions are 30% and 29.3%, respectively, which are significantly greater than 8.0% and 1.0% under high-NO_x

conditions (Ng et al., 2007; Yu et al., 2024). For the photooxidation of polycyclic aromatic hydrocarbons (PAH), Wang et al. selected the naphthalene and phenanthrene as the model systems, and measured the SOA yields of 28 ± 6.7% and 12 ± 2.6%, respectively (Wang et al., 2018). The aforementioned results show that PAH exhibit higher SOA yields compared to the toluene and styrene under high-NO_x conditions.

Corresponding descriptions have been added in the page 3 line 68-72 of the revised manuscript:

The secondary organic aerosol formation potential (SOAP) of aromatics is significantly greater than that of alkanes and alkenes during haze episodes in Beijing (Sun et al., 2016). Among these precursors, toluene is the predominant SOA-forming species, contributing more than 16% of the total SOA, followed by styrene (15%) and ethylbenzene (9.5%) (Sun et al., 2016).

2. The abstract should be comprehensible by a more general audience. There is too much context-specific information, and very little generalizable results or statements. There is also no "importance or implications of the results" as outlined in the ACP author guidelines.

Response: Based on the Editor's suggestion, the abstract has been revised to emphasize generalizable results, and a new section titled "Conclusions and atmospheric implications" has been added in the revised manuscript.

Abstract: Styrene is a highly reactive aromatic hydrocarbon that has been identified as a key secondary organic aerosol (SOA) precursor. Recent laboratory chamber experiments have identified C_7 and C_8 series compounds as the main components of SOA in the photooxidation of styrene. However, their molecular structures and formation pathways remain largely uncharacterized. Herein, the formation mechanisms of multifunctional products from the multi-generation ·OH oxidation of styrene are studied using the quantum chemistry methods. The first generation RO_2 radicals, formed through the association reaction of OH-adduct with O_2, can either proceed unimolecular decomposition to yield benzaldehyde, or undergo bimolecular reactions with HO_2 /NO to form the first generation closed-shell C_7- and C_8-products, hydroperoxide 1^{st}-ROOH ($C_8H_{10}O_3$), benzaldehyde, and organic nitrate 1^{st}-$RONO_2$ ($C_8H_9NO_3$). For the second generation ·OH oxidation, OH-addition reaction occurring at the *ortho*-site of 1^{st}-ROOH and 1^{st}-$RONO_2$ has a significant dominance. The *ortho*-OH-addition products can

proceed through two O_2-addition steps and a cyclization process to produce the peroxide bicyclic peroxy radicals (BPR). BPR can further react with HO_2 /NO to form the second generation closed-shell C_8-products, hydroperoxide 2^{nd}-ROOH ($C_8H_{12}O_8$), organic nitrate 2^{nd}-$RONO_2$ ($C_8H_{10}N_2O_{10}$), and other multifunctional products, in which the first two products have fractional yields of 41.4% and 4.8%, respectively. For the third generation OH oxidation, OH-addition occurring at the C=C double bond of 2^{nd}-ROOH and 2^{nd}-$RONO_2$ has the lowest barrier. The major third generation closed-shell C_8-products are the multifunctional hydroperoxides and organic nitrates. The volatility of the oxidation products significantly decreases with increasing the number of OH oxidation steps.

Conclusions and atmospheric implications: The results reveal that the first generation RO_2 radicals, formed from the addition of OH radicals to the C_β-site of a vinyl group in styrene followed by O_2-addition, can proceed intramolecular H-shifts to generate various alkyl and alkoxyl radicals. The rate coefficient $k_{MC\text{-}TST}$ is calculated to be 1.6×10^{-4} s^{-1}. Among the competing H-shift pathways, the hydrogen atom transfer from the –OH group to the terminal oxygen atom of the –OO group has the lowest barrier. The resulting alkoxy radical can further decompose into benzaldehyde through the successive elimination of HCHO and an OH radical. The 1,5-H shift reaction occurring at the –OH group is the rate-determining step in the formation of benzaldehyde. Alternatively, the first generation RO_2 radicals can proceed bimolecular reactions with HO_2 radicals and NO, leading to the formation of the first generation closed-shell C7- and C8-products 1^{st}-ROOH ($C_8H_{10}O_3$), benzaldehyde (C_7H_6O), and 1^{st}-$RONO_2$ ($C_8H_9NO_3$).

For the second generation OH oxidation, OH-addition reaction occurring at the *ortho*-site of 1^{st}-ROOH and 1^{st}-$RONO_2$ has a significant dominance. This is consistent with the analogous reaction systems, toluene + OH and phenol + OH, in which *ortho*-OH-addition reaction is energetically favorable (Wu et al., 2020; Xu et al., 2013). The resulting alkyl radicals may undergo two O_2-addition steps and a cyclization process to form BPR, which can react with HO_2 radicals and NO to yield the corresponding BAR, and the second generation closed-shell C8-product 2^{nd}-ROOH ($C_8H_{12}O_8$) and 2^{nd}-$RONO_2$ ($C_8H_{10}N_2O_{10}$), with the fractional yields of 41.4% and 4.8%. The unimolecular decomposition of BAR formed in the reaction 1^{st}-ROOH + OH includes two distinct pathways: (1) ring-opening and followed by decomposition, yielding the multifunctional products S10-2 ($C_4H_6O_5$) and S13 ($C_8H_{10}O_8$) with the fractional yields of 5.6% and 2.2%,

respectively; or (2) cyclization and followed by dissociation, generating the closed-shell C6-product S23 ($C_6H_6O_5$) with the fractional yield of 1.3%. The major products formed from the unimolecular decomposition of BAR in the reaction 1^{st}-$RONO_2$ + OH are the multifunctional products S30-2 ($C_4H_5NO_6$), S33 ($C_8H_{10}O_8$) and S40-1 ($C_6H_7NO_7$), with the fractional yields of 6.0%, 1.8% and 1.7%, respectively.

For the third generation OH oxidation, the addition of OH radicals to the C=C bond in 2^{nd}-ROOH and 2^{nd}-$RONO_2$ is the dominant pathway. The resulting alkyl radicals can proceed a series of reactions to produce the alkoxyl radicals, which subsequently decompose into an OH radical byproduct and a closed-shell C_8-product S47 ($C_8H_{12}O_9$), identified as the favorable pathway in the reaction 2^{nd}-ROOH + OH. S47 contains a –OOH, a peroxide bridge, two carbonyls, and three hydroxy groups. The major product formed in the reaction 2^{nd}-$RONO_2$ + OH is a closed-shell C_8-product S58 ($C_8H_{11}NO_{10}$), which contain a $–NO_3$, a peroxide bridge, two carbonyls, and three hydroxy groups. The fractional yields of S47 and S58 are 26.3% and 2.6%, respectively. The volatility of the oxidation products significantly decreases with increasing the number of OH oxidation steps in the multi-generation OH oxidation of styrene.

In the laboratory chamber experiments, the structures of some specific oxidation products remain uncharacterized but are merely inferred from the exact mass and fragmentation data. Using high-level quantum chemistry methods, we identify the molecular structures of multifunctional products and elucidate their formation pathways in the multi-generation OH oxidation of styrene. The mechanistic insights derived from this work are broadly applicable to the photooxidation of structurally analogous aromatics. Furthermore, we quantify the yields of multifunctional products and demonstrate that their volatility decreases significantly with increasing the number of OH oxidation steps. The resulting multifunctional products may undergo a series of oxidation reactions to form low volatility compounds, thereby contributing to the formation and growth of new aerosol particle. In the future, more detailed experimental and theoretical studies need to be conducted to identify the molecular structures and formation pathways of multifunctional products formed through the photooxidation of other aromatics under both low and high-NO_x conditions. These studies will facilitate a more accurate characterization of the chemical composition and formation yields of aromatic SOA, and thereby help narrow the gap between the measured and modeled SOA concentrations in urban environments.

3. Line 31-34: I do not believe this is a unique result from this study. The dominance of OH addition to vinyl group is to be expected and has been shown by other groups.

Response: As the Editor's said, pervious literatures have demonstrated that the addition of OH radicals to terminal carbon (C_{β}-site) of a vinyl group in styrene is the dominant pathway (Wang et al., 2015; Zhang et al., 2024; Wu et al., 2021). In order to avoid repetition, the related content has been removed in the abstract and conclusion sections of the revised manuscript. In the present study, we mainly focus on the formation mechanisms of multifunctional products formed from the subsequent reactions of OH-addition product in the presence of O_2 under both low- and high-NO_x conditions. The first generation RO_2 radicals, formed from the addition of OH radicals to the C_{β}-site of a vinyl group in styrene followed by O_2-addition, can proceed isomerization and bimolecular reactions with HO_2 radicals and NO to yield the first generation closed-shell products benzaldehyde (C_7H_6O), hydroperoxide 1^{st}-ROOH ($C_8H_{10}O_3$) and organic nitrate 1^{st}-$RONO_2$ ($C_8H_9NO_3$). Then, the 1^{st}-ROOH and 1^{st}-$RONO_2$ may further undergo through the multi-generation OH oxidation to yield the multifunctional products. The formation pathways and fractional yields of the major products are detailedly investigated in the present study.

4. Line 60: the term "highly oxidized" is now associated with multifunctional molecules in this field. So the listed examples are not necessarily HOMs. Please update accordingly.

Response: Based on the Editor's suggestion, the term "highly oxidized products" has been revised to "multifunctional products" in the revised manuscript.

5. Line 67: error in reference.

Response: Based on the Editor's suggestion, the related reference has been corrected in the revised manuscript.

6. I will refrain from commenting on the main body of the manuscript, as I believe the reviewers have covered those sections in their comments. However, I do encourage the authors to place their results into broader context. Two of the main conclusions make the manuscript seem like repeated work and not novel contributions: dominance of OH addition to C=C bond outside of the ring, and the formation of IVOC and LVOC from oxidation. These are quite generic

conclusions, and hardly require detailed quantum calculations to demonstrate. Broader context is needed: what is unique about these results?

Response: Based on the Editor's suggestion, the unique aspects of our findings have been added in the revised manuscript. To date, the majority of studies have focused primarily on the first generation OH oxidation mechanisms in the photooxidation of aromatic hydrocarbons (Wu et al., 2020; Xu et al., 2013; Zhang et al., 2019; Ji et al., 2017), whereas mechanistic understanding of multi-generation OH oxidation remains limited. Styrene is a highly reactive aromatic hydrocarbon and has the second-largest SOAP during haze episodes in Beijing (Sun et al., 2016). Therefore, in the present study, styrene is selected as a model compound to systematically investigate its oxidation mechanisms initiated by OH radicals under both low and high-NO_x conditions. Using high-level quantum chemistry methods, we identify the molecular structures of multifunctional products and elucidate their formation pathways in the multi-generation OH oxidation of styrene. The mechanistic insights derived from this work are broadly applicable to the photooxidation of structurally analogous aromatics. Furthermore, we quantify the yields of multifunctional products and demonstrate that their volatility decreases significantly with increasing the number of OH oxidation steps. The resulting multifunctional products may undergo a series of oxidation reactions to form low volatility compounds, thereby contributing to the formation and growth of new aerosol particle. In the future, more detailed experimental and theoretical studies need to be conducted to identify the molecular structures and formation pathways of multifunctional products formed through the photooxidation of other aromatics under both low and high-NO_x conditions. These studies will facilitate a more accurate characterization of the chemical composition and formation yields of aromatic SOA, and thereby help narrow the gap between the measured and modeled SOA concentrations in urban environments.

Corresponding descriptions have been added in the page 31 line 812-826 of the revised manuscript:

Using high-level quantum chemistry methods, we identify the molecular structures of multifunctional products and elucidate their formation pathways in the multi-generation OH oxidation of styrene. The mechanistic insights derived from this work are broadly applicable to the photooxidation of structurally analogous aromatics. Furthermore, we quantify the yields of multifunctional products and demonstrate that their volatility decreases significantly with

increasing the number of OH oxidation steps. The resulting multifunctional products may undergo a series of oxidation reactions to form low volatility compounds, thereby contributing to the formation and growth of new aerosol particle. In the future, more detailed experimental and theoretical studies need to be conducted to identify the molecular structures and formation pathways of multifunctional products formed through the photooxidation of other aromatics under both low and high-NO_x conditions. These studies will facilitate a more accurate characterization of the chemical composition and formation yields of aromatic SOA, and thereby help narrow the gap between the measured and modeled SOA concentrations in urban environments.

7. Conclusions: Please refer to the ACP author guidelines for proper presentation. Currently the conclusion section does not follow the guidelines.

Response: Based on the Editor's suggestion, the conclusion section has carefully revised in the revised manuscript.

Conclusions and atmospheric implications: The results reveal that the first generation RO_2 radicals, formed from the addition of OH radicals to the C_β-site of a vinyl group in styrene followed by O_2-addition, can proceed intramolecular H-shifts to generate various alkyl and alkoxyl radicals. The rate coefficient $k_{MC\text{-}TST}$ is calculated to be 1.6×10^{-4} s^{-1}. Among the competing H-shift pathways, the hydrogen atom transfer from the –OH group to the terminal oxygen atom of the –OO group has the lowest barrier. The resulting alkoxy radical can further decompose into benzaldehyde through the successive elimination of HCHO and an OH radical. The 1,5-H shift reaction occurring at the –OH group is the rate-determining step in the formation of benzaldehyde. Alternatively, the first generation RO_2 radicals can proceed bimolecular reactions with HO_2 radicals and NO, leading to the formation of the first generation closed-shell C7- and C8-products 1^{st}-ROOH ($C_8H_{10}O_3$), benzaldehyde (C_7H_6O), and 1^{st}-$RONO_2$ ($C_8H_9NO_3$).

For the second generation OH oxidation, OH-addition reaction occurring at the *ortho*-site of 1^{st}-ROOH and 1^{st}-$RONO_2$ has a significant dominance. This is consistent with the analogous reaction systems, toluene + OH and phenol + OH, in which *ortho*-OH-addition reaction is energetically favorable (Wu et al., 2020; Xu et al., 2013). The resulting alkyl radicals may undergo two O_2-addition steps and a cyclization process to form BPR, which can react with HO_2 radicals and NO to yield the corresponding BAR, and the second generation closed-shell C8-product

2^{nd}-ROOH ($C_8H_{12}O_8$) and 2^{nd}-$RONO_2$ ($C_8H_{10}N_2O_{10}$), with the fractional yields of 41.4% and 4.8%. The unimolecular decomposition of BAR formed in the reaction 1^{st}-ROOH + OH includes two distinct pathways: (1) ring-opening and followed by decomposition, yielding the multifunctional products S10-2 ($C_4H_6O_5$) and S13 ($C_8H_{10}O_8$) with the fractional yields of 5.6% and 2.2%, respectively; or (2) cyclization and followed by dissociation, generating the closed-shell C6-product S23 ($C_6H_6O_5$) with the fractional yield of 1.3%. The major products formed from the unimolecular decomposition of BAR in the reaction 1^{st}-$RONO_2$ + OH are the multifunctional products S30-2 ($C_4H_5NO_6$), S33 ($C_8H_{10}O_8$) and S40-1 ($C_6H_7NO_7$), with the fractional yields of 6.0%, 1.8% and 1.7%, respectively.

For the third generation OH oxidation, the addition of OH radicals to the C=C bond in 2^{nd}-ROOH and 2^{nd}-$RONO_2$ is the dominant pathway. The resulting alkyl radicals can proceed a series of reactions to produce the alkoxyl radicals, which subsequently decompose into an OH radical byproduct and a closed-shell C_8-product S47 ($C_8H_{12}O_9$), identified as the favorable pathway in the reaction 2^{nd}-ROOH + OH. S47 contains a –OOH, a peroxide bridge, two carbonyls, and three hydroxy groups. The major product formed in the reaction 2^{nd}-$RONO_2$ + OH is a closed-shell C_8-product S58 ($C_8H_{11}NO_{10}$), which contain a $–NO_3$, a peroxide bridge, two carbonyls, and three hydroxy groups. The fractional yields of S47 and S58 are 26.3% and 2.6%, respectively. The volatility of the oxidation products significantly decreases with increasing the number of OH oxidation steps in the multi-generation OH oxidation of styrene.

In the laboratory chamber experiments, the structures of some specific oxidation products remain uncharacterized but are merely inferred from the exact mass and fragmentation data. Using high-level quantum chemistry methods, we identify the molecular structures of multifunctional products and elucidate their formation pathways in the multi-generation OH oxidation of styrene. The mechanistic insights derived from this work are broadly applicable to the photooxidation of structurally analogous aromatics. Furthermore, we quantify the yields of multifunctional products and demonstrate that their volatility decreases significantly with increasing the number of OH oxidation steps. The resulting multifunctional products may undergo a series of oxidation reactions to form low volatility compounds, thereby contributing to the formation and growth of new aerosol particle. In the future, more detailed experimental and theoretical studies need to be conducted to identify the molecular structures and formation pathways of multifunctional products

formed through the photooxidation of other aromatics under both low and high-NO_x conditions. These studies will facilitate a more accurate characterization of the chemical composition and formation yields of aromatic SOA, and thereby help narrow the gap between the measured and modeled SOA concentrations in urban environments.

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