

Response to reviews

We thank the reviewers for their constructive comments that help improve the manuscript. We provide below the point-by-point responses to those comments. Reviewer comments are in **bold**. Author responses are in plain text labeled with [R]. Line numbers in the responses correspond to those in the revised manuscript with all track changes accepted. Modifications to the manuscript are in *italics*.

Reviewer #1

The manuscript by Cheng et al. investigates the formation of highly oxygenated organic molecules (HOMs) from the oxidation of benzene and toluene in a range of OH exposure and NO_x conditions generated from flow-tube based experiments. Despite a recent discovery, HOMs have received increasing attention due to their high oxygenation and low volatility thereby constituting a widespread source of SOA in the atmosphere. A number of studies have suggested HOMs can be steadily produced through the autooxidation pathway from a number of hydrocarbon precursors of both biogenic and anthropogenic origins. This is a well-motivated and timely work that examines how environmental factors impact the HOMs product distributions from the photooxidation of benzene and toluene, two hydrocarbons that have received numerous investigations in the past, yet the crucial pathways leading to SOA formation remain uncertain despite decades of investigations. Some interesting observations are presented, such as the contrasting dimer formation kinetics between the benzene and toluene systems, and the optimal [NO_x]:[HO₂] ratio that favors certain HOMs production, although the mechanism underlying these observations is elusive and warrants further evidence. Overall, it is a very detailed and interesting work. I recommend the manuscript for publication in Atmospheric Chemistry and Physics after the following comments being addressed in the revised version.

[R0] We thank the reviewer for the valuable feedback. Detailed responses are given below.

General comments:

My major comments are related to the interpretation of the trends and dynamics of the HOMs products in response to various flow tube conditions. Hundreds of HOMs products were identified in this work with the use of the ‘inlet-less’ nitrate CIMS that is highly sensitive to these ‘sticky’ molecules. It is however a great challenge to keep track of the trends and patterns of all these compounds without a good understanding of their chemical properties and formation mechanisms. I find the categorization of these compounds should be better clarified. The closed-shell products in general should include all stable products including both monomers and dimers. But it seems like here the authors use this term to specifically describe monomer products with a molecular formula of C_xH_yO_z. Perhaps ‘closed-shell

monomer products' would better represent this category.

[R1] We thank the reviewer for the suggestion. We have renamed the categories with “*closed-shell monomeric products*” and “*open-shell monomeric products*” based on the reviewer’s suggestion.

The open-shell products define all radical intermediates including both RO₂ and RO radicals. Whether these two types of radicals can be differentiated with the identified molecular formula needs to be clarified.

[R2] In this study, the monomeric species having an odd number of hydrogen atoms could be organic peroxy radicals (RO₂) and alkoxy radicals (RO). However, as noted in Line 143-146, the open-shell monomeric products observed by the NO₃⁻-TOF-CIMS in our experiments are more likely RO₂ radicals rather than RO radicals. This is because with relatively large carbon numbers, the former have lifetimes of seconds that are much longer than the latter of < 10⁻⁴ s (Orlando et al., 2003; Seinfeld and Pandis, 2016; Zhao et al., 2018). We have revised Line 142-146 to make the point more clearly.

Do these radicals ever possess higher carbon numbers (dimer-like type) than their hydrocarbon precursor?

[R3] Yes, they may. For example, if H abstraction happens to a dimer that has an even number of hydrogen atoms, a dimer-like radical with an odd number of hydrogen atoms may form. A study in the boreal forest reported ~60 gaseous dimers (C₁₆₋₂₀H_yO₆₋₉) from monoterpene oxidation with odd or even numbers of hydrogen atoms (Mohr et al., 2017). In our study, the ion intensities of dimeric products with odd hydrogen atoms are very low. We therefore only focused on dimeric products with even hydrogen atoms such as C₁₀₋₁₄H_{10,12,14,16,18,20}O₆₋₁₃ (Figure 1) which are plausibly neutral molecules formed by hydrogen-bond dimerization or cross reactions of radicals (Zhao et al., 2018). We have clarified this part in Line 170-175.

In general, the text should be clear in the formulations and definitions. While the readers appreciate categorization that certainly helps to reduce the complexity in interpreting the behaviors of hundreds of compounds, some unique information of individual species might get buried in the grouping process. I recommend the authors provide a list of the most abundant HOMs products that account for perhaps over half of the oxidized carbon in both benzene and toluene systems, along with the conditions that favor the production of each HOM compound. This would help at least elucidate dominant reaction mechanisms that govern the reaction fluxes.

[R4] The peak list and relative signal contributions (%) of major gaseous HOMs produced by the benzene and toluene oxidation experiments under low and high NO_x conditions are provided in the Supplement (Tables S2 and S3). We have revised the tables to specify the experimental conditions and revised Line 134 to clarify. The variations of selected products under different

conditions are discussed in detail in the main text related to Figures 2, 3, and 4.

On a related note, have the authors thought about the potential of using PMF analysis to help to extract typical trends and patterns of different groups of HOMs compounds?

[R5] Yes, positive matrix factorization (PMF) analysis was conducted on the unit-mass-resolution data for ions with mass-to-charge ratios (m/z) between 150 and 450 Th. As described in Sect. S2 in the Supplement, we used the PMF results to aid identification of product ions and non-product signals (Fig. S4). Three different product factors are identified. However, such temporal patterns provide limited information about the reaction kinetics and the formation mechanism of the products. So in this paper we mainly focus on some selected products that possibly represent specific reaction pathways to explore the oxidation mechanisms under a wide range of experimental conditions.

Another concern I would like to share with the authors is whether the CIMS measurements constitute sufficient information for the assignment of different functionalities to a given molecular formula based on even/odd numbers of oxygen and hydrogen atoms. HOMs produced from the autooxidation pathway are generally recognized as multi-functionalized poly peroxides. The ring-retaining oxidation chemistry of aromatics further complicates the pathways that lead to the formation of oxygenated compounds. That being said, multiple combinations of different functional groups exist for any given molecular formula with high oxygen numbers. Have the authors conducted any collision induced dissociation experiments for the HOMs molecules and identified any characteristic fragments? Without further structural information of individual HOMs molecules, the categorization of certain molecular formulas as peroxides/alcohols here seems a little handwavy.

[R6] The proposed product categories are based on (1) molecular formulas from reliable peak fitting, (2) traditional understanding of aromatic oxidation from literature, and (3) recent mechanistic developments (Mentel et al., 2015; Y. Wang et al., 2020; Garmash et al., 2020). For instance, in benzene/toluene (C_xH_y) oxidation by OH radicals, OH addition results in an alkyl radical with a formula $C_xH_{y+1}O_1$. This $C_xH_{y+1}O_1$ may quickly react with molecular oxygen (O_2) to a peroxy (RO_2) radical ($C_xH_{y+1}O_3$). The RO_2 radical $C_xH_{y+1}O_3$ can undergo endo-cyclization, where RO_2 attacks its own double bond to form an O-O bridge, resulting in a new (and more oxygenated) alkyl radical. This new alkyl radical reacts again with O_2 to form a bicyclic peroxy radical (BPR) $C_xH_{y+1}O_5$. In this pathway, compared with the parent VOC, addition of OH and two O_2 molecules changes the molecular composition by one H atom and five oxygen atoms. The BPR $C_xH_{y+1}O_5$ can undergo further autooxidation and form radicals with formula $C_xH_{y+1}O_7$. Autooxidation of RO_2 radicals involves intramolecular hydrogen shifts to the peroxide group from other carbon atoms and subsequent addition of oxygen to the produced carbon-centered radicals. The H shift itself does not modify the molecular composition, but the O_2 addition increases the oxygen content by an even number. Besides, BPR $C_xH_{y+1}O_5$ can form termination products of carbonyls ($C_xH_yO_4$),

alcohols ($C_xH_{y+2}O_4$), and hydroperoxides ($C_xH_{y+2}O_5$) (Mentel et al., 2015; Molteni et al., 2018). This means that one OH addition to the precursor C_xH_y could lead to termination products with hydrogen numbers of y and $y+2$. When the second OH attack occurs, products with hydrogen numbers of $< y$ and $> y+2$ may be produced by multi-generation OH reactions (Table R1). With such established knowledge, some product formulae are associated with specific pathways. Some product formulae however may involve multiple pathways that we cannot differentiate (e.g., y , $y+1$, and $y+2$ products in Table R1). In this case, the collision induced dissociation (CID) experiments may be very helpful but we have not conducted such experiments to further explore possible structures of the HOM molecules like what have done in a recent study (Zaytsev et al., 2019a). Our discussion about the formation mechanisms are mainly made for those products that are associated with specific pathways. To clarify, we have included information regarding this in Line 120-132 and Line 265-267.

Table R1. Potential product formulae (oxygen number ≥ 5) from a second OH attack in benzene and toluene oxidation.

Second OH attack	H_{y-} series products		H_{y+2-} series products	
	H abstraction	OH addition	H abstraction	OH addition
	Hydrogen number		Hydrogen number	
Radical	$y-1$	$y+1$	$y+1$	$y+3$
Carbonyl	$y-2$	y	y	$y+2$
Alcohol	y	$y+2$	$y+2$	$y+4$
Hydroperoxide	y	$y+2$	$y+2$	$y+4$

I have a similar impression about whether the CIMS measurements alone are sufficient to drive the mechanisms discussed in the text, or rather using established mechanisms to rationalize the observations. For example, the authors highlight that ‘multi-generation OH oxidation plays an important role in the product distribution, which likely proceeds more preferably via H subtraction than OH addition for early-generation products from light aromatics’.

[R7] By applying the principles outlined in [R6] above, we may expect products with hydrogen number (y) shown in Table R1 from multi-generation OH reaction (e.g., the second OH attack) on the first-generation products from the initial reactions of VOCs with OH radicals. In multi-generation OH oxidation of the first-generation products, when the second OH attack occurs on a product that contains a hydrogen number of y via H abstraction, termination products with hydrogen numbers $< y$ should be formed. Similarly, when the second OH attack occurs on a product that contains a hydrogen number of $y+2$ via OH addition, termination products with hydrogen numbers $> y+2$ should be formed. For OH addition to occur, the first-generation closed-shell molecules must still contain a carbon–carbon double bond in their structure (Garmash et al., 2020). The contributions of a third OH attack to the total of detected signals are often low (Molteni et al., 2018). We have added Table R1 into the Supplement as Table S5 and revised Line 265-267 and

Line 276-277 to clarify. We have also added in Line 289-290 to clarify that our interpretation is made on the basis of current mechanistic understanding of aromatic oxidation.

Indeed, recent studies have proposed a unique pathway in the aromatic oxidation process, i.e., the ring-retaining chemistry that constantly takes up oxygen in the aromatic ring. The relevance and importance of this branch in the experimental conditions (e.g., high HO_x intensities) of the present work needs to be explicitly discussed.

[R8] Following the reviewer's suggestion, we have added discussions in the main text in Line 159-164: "*BPRs (i.e., C₆H₇O₅ from benzene oxidation and C₇H₉O₅ from toluene oxidation) can undergo unimolecular isomerization reactions to form more oxidized peroxy radicals, which compete with bimolecular reactions (Wang et al., 2017). The relative greater signal intensities of ring-retaining O₇ or O₉ HOM monomers compared with O_{<6} ones suggest that the termination of RO₂ by HO₂ and the phenol oxidation pathway are perhaps relatively less important than the autooxidation pathway under experimental conditions herein (Calvert et al., 2002; Schwantes et al., 2017; Garmash et al., 2020)*". For the importance of phenol-pathway and auto-oxidation pathway, we add also added the following information in Sect.S1 in the Supplement as follows: "*Reactions of the newly formed phenols (e.g., cresol from toluene) can again be initiated by OH radicals, which have rate constants one order of magnitude higher than those of the aromatic precursors. Studies have shown that a major fraction of oxygenated compounds through this pathway has oxygen atoms less than 6 (Calvert et al., 2002; Schwantes et al., 2017; Garmash et al., 2020).*"

In addition, the extent of OH exposure directly determines the number of RO₂ formed and consequently the likelihood of autooxidation that leads to HOMs production, but whether OH oxidation proceeds via abstraction or addition seems not directly supported by the observations presented in the text.

[R9] As replied in [R7], products with hydrogen numbers of < y are most likely formed via H abstraction, while those with hydrogen numbers of > y+2 are from OH addition on the basis of current mechanistic understanding (Table R1). We did not focus on the y, y+1, and y+2 products that may be involved in both H abstraction and OH addition. Therefore, we think our results of the increasing fractions of y-2 products but decreasing fractions of y+4 products for increasing OH exposures as well as the monotonically increasing concentration of y-2 products may suggest that the multi-generation OH oxidation may proceed preferably via H subtraction than OH addition for early-generation products. Garmash et al. (2020) also noted that higher OH concentrations caused a larger variety in HOM products, with H-abstraction oxidation becoming more significant. We have added this point in Line 290-291 in addition to the revisions made in [R7].

Specific comments:

- Line 15: This is a vague statement. Is there any unique feature of the OFR system used here

that likely promotes the HOMs formation compared with previous studies? or just simply based on the longer residence time / slower flow rate?

[R10] The comparison of previous flow-tube experiments with our study are discussed in detail in Sect. 3.2, which includes several aspects not just simply based on the residence time. We have revised this sentence in abstract in Line 15 as follows: “*More oxygenated products present in our study than in previous flow-tube studies, highlighting the impact of experimental conditions on product distributions.*”

- Line 185: It is interesting to see that ‘the concentrations of fragmented, closed-shell and open-shell products first increase and then slightly decrease with the increasing OH exposure’ for the toluene case. Have the authors thought about any potential fragmentation process that breaks these HOMs molecules apart?

[R11] The fragmented products with carbon numbers less than their precursors may be formed by ring-scission (e.g., Scheme S2 in SI) that breaks the aromatic ring apart to form dicarbonyls and epoxy-dicarbonyl (Zaytsev et al., 2019b). In addition, some fragmented products can be formed through CO elimination from an acyl radical (Rissanen et al., 2014), splitting CO₂ from an RO radical (Garmash et al., 2020), or dealkylation (Birdsall and Elrod, 2011). We have added this information in Line 136-138.

- Line 190: Responses of the dimer products to increasing OH oxidation of toluene was found different compared with the benzene system. While the presence of the methyl branch on the aromatic ring might play a role in fragmentation, it is ultimately the RO₂ self/cross combination process that results in the dimer formation. Have the authors compared the relative increases in both RO₂ and HO₂ levels in response to the increasing OH exposure in the benzene and toluene oxidation experiments?

[R12] One potential contributor to the difference of the dependence of dimer formation on OH exposure is the more significant elevated RO₂ concentrations (0.2 to 0.9 pptv) as the OH exposure increases for benzene oxidation than those (0.3 to 0.5 pptv) for toluene oxidation while the HO₂ concentrations in the two sets of experiments are similar (1.5-2.4 ppbv). The enhancement of RO₂ concentrations may promote the dimer formation through the self or cross reactions of RO₂ (Mohr et al., 2017). On the other hand, a previous study indicates that the accretion of RO₂ depends on the functional groups of the RO₂ (Berndt et al., 2018). Whether the decreasing concentrations of dimeric products with OH exposure is related to the steric effects of the substituted methyl group of toluene requires further investigations. We have added the above discussion in Line 216-224.

- Line 195-200: Functionalities cannot be simply inferred here solely based on the molecular formula without any additional structural information. Another layer of uncertainty that adds to the level of complexity is the rates and number of generations of autooxidation pathways.

[R13] We agree with the reviewer that the interpretation of the closed-shell products are only possibilities. Given the added mechanistic information in the revised manuscript as replied in [R6], we know BPRs may form $C_xH_{y+2}O_{5,7}$ hydroperoxides, $C_xH_yO_{4,6}$ carbonyls, and $C_xH_{y+2}O_{4,6}$ alcohols. But the detected $C_xH_{y+2}O_{5,7}$ do not have to be hydroperoxides. We have revised the description here in Line 232-239 as follows: *“As described in Sect. 3.1, the further reactions of $C_xH_{y+1}O_5$ and $C_xH_{y+1}O_7$ may form closed-shell monomers such as hydroperoxides ($C_xH_{y+2}O_{5,7}$), carbonyls ($C_xH_yO_{4,6}$), and alcohols ($C_xH_{y+2}O_{4,6}$) (Mentel et al., 2015; Molteni et al., 2019), although these formulae may correspond to other functionalities depending on the reaction rates and numbers of generation of autooxidation pathways. For multiple steps of auto-oxidation of BPRs or RO_2 radicals ($C_xH_{y+1}O_5$ or $C_xH_{y+1}O_7$), the products with two more hydrogen atoms than the precursor are plausibly hydroperoxides ($C_xH_{y+2}O_z$) if z is an odd number and alcohols if an even number. On the other hand, products that have the same hydrogen atoms ($C_xH_yO_z$) are likely carbonyls with an even number of z . Instead, if the carbonyl formation involves the RO pathway, $C_xH_yO_z$ with an odd number of z may be formed.”*

- Line 245: Another factor playing in here might be the much slower reaction rate of benzene toward OH radicals.

[R14] We thank the reviewer for this suggestion. We have revised in Line 282-286 as follows: *“The decreasing trends at high OH exposures are more significant for toluene-derived products. Such differences might be explained by (1) the faster OH+VOC rate for toluene than for benzene and (2) the methyl group in toluene as well as the added -OH groups during oxidation that may increase the electron density on the aromatic ring through a resonant electron-donating effect and thereby activate the aromatic ring and facilitate further addition reactions to form products with multiple -OH groups (M. Wang et al., 2020).”*

- Line 255: The authors need to provide more details about how the wall losses in flow tube and sampling lines are corrected in the molar yield calculations.

[R15] The details for the wall loss corrections of HOMs are provided in Sect. S4 in the Supplement. We have added some information to Line 296-299 as follows: *“To calculate the molar yields of HOM products, wall losses are corrected, including the loss in the sampling line, the loss to the OFR walls estimated by eddy diffusion, the loss to aerosol particles in the OFR (i.e., the condensation sink calculated on the basis of particle measurements), and the loss to non-condensable products due to continuous reaction with OH (Palm et al., 2016). Details are provided in Sect. S4 in the Supplement.”*

- Line 282: How does the OH level change along with varying $[NO_x]:[HO_2]$ ratios?

[R16] The OH concentrations decreased from 0.19 ppb (1.1% vol N_2O) to 0.05-0.12 ppb (4.4% vol N_2O) for benzene and from 0.21 ppb (1.1% vol N_2O) to 0.05-0.12 ppb (4.4% vol N_2O) for toluene. This change of a factor of 2 to 4 is much smaller than the variation of $[NO_x]:[HO_2]$ ratio

(i.e., a factor of 3 to 18).

- Line 335: There have been a few numbers of recent studies demonstrating the formation of HOMs from the oxidation of alkyl-aromatics. This is a good place to summarize how the present study contribute to new insights into this system and what makes this study unique compared with previous studies.

[R17] We thank the reviewer for the suggestion. We have added the following summary in Line 383-387: *“In this study, we investigated the formation of HOMs in the OFR by the oxidation of benzene and toluene in a wide range of OH exposure and NO_x conditions. Recent findings emphasize the significance of the bicyclic channel in the oxidation of light aromatics (Wang et al., 2017; Molteni et al., 2018; Tsiligiannis et al., 2019; Garmash et al., 2020; Y. Wang et al., 2020). The presence of NO_x enhances the formation of organonitrates and even dinitrate organic compounds. Extensive autoxidation and accretion reaction has been reported for substituted aromatics (Y. Wang et al., 2020).”*

References:

- Berndt, T., Scholz, W., Mentler, B., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion product formation from self- and cross-reactions of RO₂ radicals in the atmosphere, *Angew. Chemie*, 57, 3820-3824, <https://doi.org/10.1002/anie.201710989>, 2018.
- Birdsall, A. W., and Elrod, M. J.: Comprehensive NO-dependent study of the products of the oxidation of atmospherically relevant aromatic compounds, *J. Phys. Chem. A*, 115, 5397-5407, <https://doi.org/10.1021/jp2010327>, 2011.
- Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G. Y.: *The mechanisms of atmospheric oxidation of aromatic hydrocarbons*, Oxford University Press, New York, 2002.
- Garmash, O., Rissanen, M. P., Pullinen, I., Schmitt, S., Kausiala, O., Tillmann, R., Zhao, D., Percival, C., Bannan, T. J., Priestley, M., Hallquist, Å. M., Kleist, E., Kiendler-Scharr, A., Hallquist, M., Berndt, T., McFiggans, G., Wildt, J., Mentel, T. F., and Ehn, M.: Multi-generation OH oxidation as a source for highly oxygenated organic molecules from aromatics, *Atmos. Chem. Phys.*, 20, 515-537, <https://doi.org/10.5194/acp-20-515-2020>, 2020.
- Mentel, T. F., Springer, M., Ehn, M., Kleist, E., Pullinen, I., Kurtén, T., Rissanen, M., Wahner, A., and Wildt, J.: Formation of highly oxidized multifunctional compounds: autoxidation of peroxy radicals formed in the ozonolysis of alkenes – deduced from structure–product relationships, *Atmos. Chem. Phys.*, 15, 6745-6765, <https://doi.org/10.5194/acp-15-6745-2015>, 2015.
- Mohr, C., Lopez-Hilfiker, F. D., Yli-Juuti, T., Heitto, A., Lutz, A., Hallquist, M., D'Ambro, E. L., Rissanen, M. P., Hao, L., Schobesberger, S., Kulmala, M., Mauldin III, R. L., Makkonen, U., Sipilä, M., Petäjä, T., and Thornton, J. A.: Ambient observations of dimers from terpene oxidation in the gas phase: Implications for new particle formation and growth, *Geophys. Res. Lett.*, 44, 2958-2966, <https://doi.org/10.1002/2017gl072718>, 2017.

Molteni, U., Bianchi, F., Klein, F., El Haddad, I., Frege, C., Rossi, M. J., Dommen, J., and Baltensperger, U.: Formation of highly oxygenated organic molecules from aromatic compounds, *Atmos. Chem. Phys.*, 18, 1909-1921, <https://doi.org/10.5194/acp-18-1909-2018>, 2018.

Molteni, U., Simon, M., Heinritzi, M., Hoyle, C. R., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke, S., Dias, A., Duplissy, J., Frege, C., Gordon, H., Heyn, C., Jokinen, T., Kuerten, A., Lehtipalo, K., Makhmutov, V., Petaja, T., Pieber, S. M., Praplan, A. P., Schobesberger, S., Steiner, G., Stozhkov, Y., Tome, A., Trostl, J., Wagner, A. C., Wagner, R., Williamson, C., Yan, C., Baltensperger, U., Curtius, J., Donahue, N. M., Hansel, A., Kirkby, J., Kulmala, M., Worsnop, D. R., and Dommen, J.: Formation of highly oxygenated organic molecules from α -pinene ozonolysis: chemical characteristics, mechanism, and kinetic model development, *ACS Earth Space Chem.*, 3, 873-883, <https://doi.org/10.1021/acsearthspacechem.9b00035>, 2019.

Orlando, J. J., Tyndall, G. S., and Wallington, T. J.: The atmospheric chemistry of alkoxy radicals, *Chem. Rev.*, 103, 4657-4690, <https://doi.org/10.1021/cr020527p>, 2003.

Palm, B. B., Campuzano-Jost, P., Ortega, A. M., Day, D. A., Kaser, L., Jud, W., Karl, T., Hansel, A., Hunter, J. F., Cross, E. S., Kroll, J. H., Peng, Z., Brune, W. H., and Jimenez, J. L.: In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor, *Atmos. Chem. Phys.*, 16, 2943-2970, <https://doi.org/10.5194/acp-16-2943-2016>, 2016.

Rissanen, M. P., Kurtén, T., Sipilä, M., Thornton, J. A., Kangasluoma, J., Sarnela, N., Junninen, H., Jørgensen, S., Schallhart, S., Kajos, M. K., Taipale, R., Springer, M., Mentel, T. F., Ruuskanen, T., Petäjä, T., Worsnop, D. R., Kjaergaard, H. G., and Ehn, M.: The formation of highly oxidized multifunctional products in the ozonolysis of cyclohexene, *J. Am. Chem. Soc.*, 136, 15596-15606, <https://doi.org/10.1021/ja507146s>, 2014.

Schwantes, R. H., Schilling, K. A., McVay, R. C., Lignell, H., Coggon, M. M., Zhang, X., Wennberg, P. O., and Seinfeld, J. H.: Formation of highly oxygenated low-volatility products from cresol oxidation, *Atmos. Chem. Phys.*, 17, 3453-3474, <https://doi.org/10.5194/acp-17-3453-2017>, 2017.

Seinfeld, J. H., and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Third Edition, John Wiley & Sons, Inc., Hoboken, New Jersey, 2016.

Tsiligiannis, E., Hammes, J., Salvador, C. M., Mentel, T. F., and Hallquist, M.: Effect of NO_x on 1,3,5-trimethylbenzene (TMB) oxidation product distribution and particle formation, *Atmos. Chem. Phys.*, 19, 15073-15086, <https://doi.org/10.5194/acp-19-15073-2019>, 2019.

Wang, M., Chen, D., Xiao, M., Ye, Q., Stolzenburg, D., Hofbauer, V., Ye, P., Vogel, A. L., Mauldin, R. L., Amorim, A., Baccarini, A., Baumgartner, B., Brilke, S., Dada, L., Dias, A., Duplissy, J., Finkenzeller, H., Garmash, O., He, X., Hoyle, C. R., Kim, C., Kvashnin, A., Lehtipalo, K., Fischer, L., Molteni, U., Petäjä, T., Pospisilova, V., Quéléver, L. L. J., Rissanen, M. P., Simon, M., Tauber, C., Tomé, A., Wagner, A. C., Weitz, L., Volkamer, R., Winkler, P. M., Kirkby, J., Worsnop, D. R., Kulmala, M., Baltensperger, U., Dommen, J., El Haddad, I., and Donahue, N. M.: Photo-oxidation of aromatic hydrocarbons produces low-volatility organic compounds, *Environ.*

Sci. Technol., <https://doi.org/10.1021/acs.est.0c02100>, 2020.

Wang, S., Wu, R., Berndt, T., Ehn, M., and Wang, L.: Formation of highly oxidized radicals and multifunctional products from the atmospheric oxidation of alkylbenzenes, *Environ. Sci. Technol.*, 51, 8442-8449, <https://doi.org/10.1021/acs.est.7b02374>, 2017.

Wang, Y., Mehra, A., Krechmer, J. E., Yang, G., Hu, X., Lu, Y., Lambe, A., Canagaratna, M., Chen, J., Worsnop, D., Coe, H., and Wang, L.: Oxygenated products formed from OH-initiated reactions of trimethylbenzene: autoxidation and accretion, *Atmos. Chem. Phys.*, 20, 9563-9579, <https://doi.org/10.5194/acp-20-9563-2020>, 2020.

Zaytsev, A., Breitenlechner, M., Koss, A. R., Lim, C. Y., Rowe, J. C., Kroll, J. H., and Keutsch, F. N.: Using collision-induced dissociation to constrain sensitivity of ammonia chemical ionization mass spectrometry (NH₄⁺ CIMS) to oxygenated volatile organic compounds, *Atmos. Meas. Tech.*, 12, 1861-1870, <https://doi.org/10.5194/amt-12-1861-2019>, 2019a.

Zaytsev, A., Koss, A. R., Breitenlechner, M., Krechmer, J. E., Nihill, K. J., Lim, C. Y., Rowe, J. C., Cox, J. L., Moss, J., Roscioli, J. R., Canagaratna, M. R., Worsnop, D. R., Kroll, J. H., and Keutsch, F. N.: Mechanistic study of the formation of ring-retaining and ring-opening products from the oxidation of aromatic compounds under urban atmospheric conditions, *Atmos. Chem. Phys.*, 19, 15117-15129, <https://doi.org/10.5194/acp-19-15117-2019>, 2019b.

Zhao, Y., Thornton, J. A., and Pye, H. O. T.: Quantitative constraints on autoxidation and dimer formation from direct probing of monoterpene-derived peroxy radical chemistry, *Proc. Natl. Acad. Sci. U. S. A.*, 115, 12142-12147, <https://doi.org/10.1073/pnas.1812147115>, 2018.