Author’s response:

We thank the Referee for the careful revision and comments, which helped improving the overall quality of the manuscript.
A point-by-point answer to the referee’s remarks is detailed in the following (in black the referee comments, in blue our answers, in green text modifications)

The authors describe experimental findings from a flow-tube study on HOM formation from the reaction of OH radicals with a series of aromatic compounds. OH radicals were generated by water VUV photolysis at 172 nm. The OH+aromatic reaction carried out in a flow system was separated from the OH radical production. Nitrate CIMS was chosen for HOM detection. OH radical concentrations in the system were obtained using an indirect way via a scavenger method. HOM formation from aromatic compounds represents an interesting topic within the framework of SOA precursor formation. It could be a very important process for SOA formation in urban areas. This manuscript needs a couple of clarifications and further explanations before publication can be recommended. Here my comments:

Line 17: From my perspective, the authors do not present “identified products”, they simply show product signals and they discuss possible moieties or structural elements of these products.
We agree that not the chemical structures but only the molecular formulas of the HOMs were identified. We modified the text accordingly:
We report the elemental composition of the HOMs and show the differences in the oxidation patterns of these ArHCs.

Line 48: It is better to say: “aromaticity is lost (or is abrogated)”
We agree and we modified this:
When the aromaticity is lost by the OH addition, non-aromatic double bonds are …

Line 65: OH radicals were generated by water photolysis using a Xe excimer lamp. The atmospheric chemistry community does not commonly use this approach of OH formation. It should be explained here more in detail what are the main reaction steps in a water/air mixture after irradiation at 172 nm. I guess it is also important to comment on the formation of other products like HO2, H2O2 and ozone and their concentration levels in the reaction gas. How important is especially the reaction of OH radicals with HO2 before entering the mixing zone with the flow containing the aromatic compound? It is not enough to state some references only.
We include in the appendix section (Appendix C) a description of the OH radical formation with the Xe excimer lamp and a model of the chemistry in these experiments.

Appendix C
The radiation at 172 nm excites molecular oxygen and water vapor triggering the following radical reactions:

\[
\begin{align*}
hv + O_2 & \rightarrow O(^1D) + O(^3P) & \text{(R-C1)} \\
O(^1D) + M & \rightarrow O(^3P) + M & \text{(R-C2)} \\
O(^3P) + O_2 + M & \rightarrow O_3 + M & \text{(R-C3)} \\
O(^1D) + H_2O & \rightarrow 2 OH & \text{(R-C4)} \\
hv + H_2O & \rightarrow H + OH & \text{(R-C5)} \\
H + O_2 + M & \rightarrow HO_2 + M & \text{(R-C6)} \\
OH + O_3 & \rightarrow HO_2 + O_2 & \text{(R-C7)} \\
HO_2 + O_3 & \rightarrow OH + 2O_2 & \text{(R-C8)} \\
OH + HO_2 & \rightarrow H_2O + O_2 & \text{(R-C9)} \\
HO_2 + HO_2 & \rightarrow H_2O_2 + O_2 & \text{(R-C10)} \\
H_2O_2 + OH & \rightarrow H_2O + HO_2 & \text{(R-C12)}
\end{align*}
\]
The humidified air flow is exposed to the 172 nm radiation for 50 ms and is then within 30 ms transferred to the mixing zone with the sample flow. The oxidant species produced are OH, HO$_2$, O$_3$ and H$_2$O$_2$. The final OH concentration entering the mixing zone depends on the residence time in the lamp and in the transfer region.

The kinetic model includes 31 species and 36 reactions from the MCM 3.3.1 (Jenkin et al., 2003). Mesitylene is selected as ArHC for these simulations and its reaction mechanism is extended up to the second generation products. The model is run for 20 seconds in agreement with the residence time of the flow tube reactor with a simulation time resolution of 2 ms. The model is initiated with the measured concentrations of ozone (3.45 $10^{12}$ molecules cm$^{-3}$ without mesitylene) and mesitylene (2.46 $10^{12}$ molecules cm$^{-3}$ without lamp on) at the exit of the flow tube. The initial OH radical concentration (8.50 $10^{11}$ molecules cm$^{-3}$) is tuned in order to match the OH exposure, which was determined from the amount of reacted mesitylene. The initial HO$_2$ radical concentration (1.70 $10^{12}$ molecules cm$^{-3}$) is set at twice the initial OH radical concentration. Wall losses of about 35% are estimated for mesitylene HOMs but are not implemented in the model. Figure C1 shows the temporal evolution of 6 selected species: reacted mesitylene (T135MB reacted), HO$_2$ radical (HO2), OH radical (OH) as well as 3 products of the mesitylene oxidation with the OH radical (TM135BPRO2, TM135BPOOH and TM135B2OH). TM135BPRO2 is an intermediate peroxy radical after OH attack; TM135BPOOH is a product from the reaction of TM135BPRO2 with the HO$_2$ radical while TM135BPO2OH is a product from the reaction of TM135BPRO2 with a peroxy radical RO$_2$. Mesitylene reacted reaches a plateau after about 0.03 seconds while TM135BPRO2 reaches a maximum value around 0.01-0.02 seconds and then rapidly decreases. The closed shell products TM135BPOOH and TM135BPO2OH constantly increase and reach a plateau after about 0.4-1.0 seconds. A similar trend could be expected for HOMs assuming that TM135BPRO2 undergoes an autoxidation chain and is terminated either by HO$_2$ or by RO$_2$. In a test run where the initial mesitylene concentration and the reaction rate constant towards OH radicals were doubled, the ratio TM135BPOOH/TM135BPO2OH varied only by about 18%.
Line 81: Obviously, the reagent ion spectrum showed a strong signal of trifluoroacetate arising from fluorinated contaminants of the Nafion membrane. Was there also a strong signal of the “dimer”, i.e. the trifluoroacetate adduct with trifluoroacetic acid? It would be fine to see a reagent ion spectrum as recorded for commonly used reaction conditions (maybe in Appendix). Was the trifluoroacetate concentration low enough that a possible contribution in the ionization process can be excluded?

The main source of trifluoroacetate is indeed the Nafion membrane. Additional experiments (not presented here) with a bubbler showed a much lower trifluoroacetate signal. The trifluoroacetate monomer was the main peak followed by the adduct with nitric acid and the trifluoroacetate dimer. In the experiments where the trifluoroacetate signal was rather high we did not observe adducts with HOMs. From this we conclude that trifluoroacetate did not influence the ionization of the analyte.

Line 84: What was the procedure applied for the determination of the “average” OH radical concentration? Was the disappearance of deuterated butanol monitored by PTR-MS when OH formation was switched on? What was the initial butanol concentration? I guess it has been done in absence of the aromatics, or not? The authors used a kind of a discharge technique. Consequently, the initial OH concentration was much higher than the “average” concentration of 1.9x10(8) molec./cc.? Please provide more information. In addition, the authors could show a figure with OH, aromatic and total HOM concentrations as a function of time or reactor length.

The OH concentration was determined from the difference in precursor concentration between excimer lamp switched on or off. Two D9-butanol, toluene, mesitylene, and biphenyl experiments resulted in an average value of 2 10^8 OH radicals cm^3. It was not possible to derive an OH
concentration from the benzene, ethylbenzene and naphthalene experiments due to technical difficulties. As xylene was a mixture of 3 isomers with different OH-reaction rate constants, the OH concentration could not be determined. We assume that the OH production was constant in all experiments as the lamp was operated under similar conditions. We developed a kinetic model to simulate the decrease of the aromatic compounds under the conditions of our flow tube experiments. This is described in the appendix (Appendix section C), which includes a figure with the concentrations of OH, aromatic precursor and a HOM representative as a function of time (see description above).

Line 92: At this point it is not clear where the (molar?) HOM formation yields are coming from? Did the authors measure the disappearance of the aromatics by PTRMS, if measureable? Or did the authors calculate the amount of converted aromatics based on their measured OH radical concentration? The concentrations of converted aromatics along with the total HOM concentrations should be stated in Table 1 or in a separate table. What was the calibration factor used for the HOM concentrations measured by nitrate CIMS, where does it come from and what is the detection limit for these HOMs? Please clarify the way of concentration determination for reacted aromatics as well as for the HOMs.

The HOM molar yield was calculated from the ratio of HOM concentration to reacted ArHC (the yields were not corrected for the HOMs losses). The amount of ArHC reacted was calculated based on the assumption, that the OH production was similar in all experiments (see comment above). The HOMs quantification is based on the calibration factor for sulfuric acid and the assumption that HOMs have the same ionization efficiency as sulfuric acid (Ehn et al., 2014; Kirkby et al., 2016). It is known that the ionization efficiency depends on the structure of the HOMs. Since the ionization efficiency might be <1 for some HOM structures, the reported concentrations here represent lower limits. We added the following in the text:

HOMs yields are calculated as the ratio of HOMs measured to ArHC reacted. HOMs were quantified using the calibration factor for sulfuric acid and assuming the same charging efficiency for HOMs (Ehn et al., 2014; Kirkby et al., 2016). From the decrease of the precursor concentration (lights off versus lights on) we determined an average OH concentration. From the experiments with D9-butanol, toluene, mesitylene and biphenyl an average OH concentration of 2 10^8 OH cm^-3 was obtained. Assuming the same OH production of the lamp in all experiments ArHC reacted was calculated from the OH radical exposure using the reaction rate coefficients at 25°C.

Table 1 was complemented with HOMs concentration, reacted fraction of ArHCs and HOMs yield and looks now like this:

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (molecules cm^-3)</th>
<th>k_{OH} (10^{-12} cm^3 molecules^-1 s^-1)</th>
<th>Reacted fraction (%)</th>
<th>[HOM] (molecules cm^-3)</th>
<th>HOMs yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene (C_6H_6)</td>
<td>9.85 \times 10^{13}</td>
<td>1.22</td>
<td>0.5</td>
<td>1.2 \times 10^9</td>
<td>0.2</td>
</tr>
<tr>
<td>Toluene (C_7H_8)</td>
<td>1.97 \times 10^{13}</td>
<td>5.63</td>
<td>2.3</td>
<td>4.4 \times 10^8</td>
<td>0.1</td>
</tr>
<tr>
<td>Ethylbenzene (C_8H_{10})</td>
<td>1.13 \times 10^{13}</td>
<td>7.0</td>
<td>2.8</td>
<td>9.4 \times 10^8</td>
<td>0.3</td>
</tr>
<tr>
<td>Compound</td>
<td>(k) (10^{13})</td>
<td>(k) (10^{12})</td>
<td>(k) (10^{9})</td>
<td>(k) (10^{3})</td>
<td></td>
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<td>-------------------------</td>
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<td></td>
</tr>
<tr>
<td>(o/m/p) - xylene ((C_8H_{10}))</td>
<td>2.95</td>
<td>23.1/14.3</td>
<td>2.8</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Mesitylene ((C_{9}H_{12}))</td>
<td>2.46</td>
<td>56.7</td>
<td>3.1</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Naphthalene ((C_{10}H_{8}))</td>
<td>2.95</td>
<td>23.0</td>
<td>1.4</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Biphenyl ((C_{12}H_{10}))</td>
<td>4.43</td>
<td>7.1</td>
<td>1.8</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

Reference for the \(k\)-rates: (Atkinson and Arey, 2003)

Line 95 and Fig. 2: Main peaks in Fig. 2 should be numbered and this numbering should be also given in the corresponding signal table in Appendix. It makes it easier to understand the signal assignment.
We updated Figure 2 by adding for each compound the chemical structure on the left side of the figure. To help the reader we included labels with the oxygen number in the monomer and dimer panels.
See Figure 2.

Line 110 and Table 2: The detected product distribution is strongly dependent on the reaction conditions and, therefore, only valid for the conditions of this experiment. That should be clearly mentioned at this point.
We agree with this. The new text reads:
However, since the mass-dependent ion transmission efficiency is rather smooth the given values may faithfully represent the relative product distribution of the different aromatic compounds.

Line 124: What does it mean “more oxygenated radicals have a higher probability to undergo an auto-termination radical reaction”? Please state this pathway and give more information for that.
This statement can be derived from (Rissanen et al., 2014): We rewrote it as follows:
Additionally, more oxygenated radicals have a higher probability to undergo a unimolecular termination compared to a radical-radicale recombination \((\text{RO}_2\cdot + \text{RO}_2\cdot \text{ or } \text{RO}_2\cdot + \text{HO}_2\cdot)\). More oxygen atoms imply more peroxy functional groups and therefore a higher probability of a hydrogen abstraction in geminal position of a peroxide which results in an OH radical loss and a carbonyl group formation.

Line 161: Do the authors believe that they are able to detect RO radicals by nitrate CIMS? What is the expected RO lifetime with respect to isomerization and for a possible reaction with O2 (depending on the structure)?
We do not detect alkoxy radicals. Based on our understanding their lifetime is too short to yield detectable concentrations. From the fact that compounds with even numbers of oxygen are observed we infer that the alkoxy radical isomerizes to a carbon centered radical and takes up oxygen molecules in an auto-oxidation mechanism. This is explained in the text in the lines 166-168.

Line 167: “uptake an oxygen atom”? We replaced atom with molecule, can again take up an oxygen molecule.

Line 223: At the end of this paragraph a discussion on possible ozone reactions of products is welcome. The ozone concentration in this experiment is quite high and the products have to
contain double bonds after losing the aromaticity. Moreover, a statement is needed how the results of this study can be used to explain the formation of SOA precursors for urban conditions where the reaction of RO$_2$+NO dominates the RO$_2$ fate in most cases.

While the ArHC do not react with ozone, oxidation products with remaining double bonds indeed may. The ozone concentration produced in the Xe excimer lamp is about 140 ppb. The residence time in the flow tube is 20 s. Reaction rate constants for the ozonolysis of alkenes are in the range of $10^{-16} – 10^{-18}$ cm$^3$ molecule$^{-1}$s$^{-1}$. Under the condition that 20 ppb of ArHC have reacted and yield 10% of products with a double bond still containing the carbon skeleton of the parent molecule, about 0.14 - 14 ppt of these products will react with ozone. Assuming a high HOMs yield of 10% from this ozonolysis reaction we can expect 0.014-1.4 ppt of HOMs from ozonolysis. This can be compared to 60-800 ppt HOMs produced via OH radical attack. Thus, the contribution of ozonolysis to HOMs formation can be neglected.

We added the following to the text:

Under urban conditions, in the presence of NO, the reaction of RO$_2$+NO will compete with the autoxidation pathway. This can lead to relatively highly oxygenated nitrates of low volatility or oxyradicals. The latter can isomerize to a carbon centered radical as under our conditions and again undergo autoxidation. Highly oxygenated organic nitrates have been recently identified in SOA (Lee et al., 2016). While this study shows that autoxidation can also occur after an OH attack of ArHC, the formation of low volatility products via this route in the presence of NO, which is typical of urban atmospheres, needs further investigation.

First generation oxidation products may still contain carbon-carbon double bonds, which could also further react with ozone forming more highly oxygenated products. Since the reaction time is very short in the flow tube this reaction is negligible but could be another potential pathway in the ambient atmosphere.

Fig.5: What does “Product with DB” mean?
DB means products with double bonds.
This is now mentioned in Figure 5.
References


Nakao, S., Clark, C., Tang, P., Sato, K. and Cocker, D.: Secondary organic aerosol formation from phenolic compounds in the absence of NOx, Atmos. Chem. Phys., 11(20), 10649–10660,


