

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)

Significance This is an interesting work describing the important observation of highly oxidized molecules (HOM) from aromatic oxidation reactions. Although certainly important observation in a current "hot-topic" field, and as such should merit its publication, I have a problem how the results are presented. It almost seems as this has been written with a format more suitable for general wider audience in a magazine format, and not really addressed to the atmospheric chemist and physics community. I feel that a certain amount of details of the experiments and the setup have been omitted, which could greatly help researchers in the field performing these type of experiments. Due to this formatting issue in many cases it seems that the text just assumes too much from the reader. This will become clearer from the large amount of specific comments given below and starting with: "What do you mean by..". So while I find the topic extremely interesting and the finding important, I cannot recommend publication in the current form. I further stress that most of this is due to the current presentation form and all of the problems can be fixed relatively easily. Thus I strongly suggest that the authors take time to modify/rewrite the text according to the comments given below, after which I can recommend publishing.

Major Comments:

Abstract should contain the major details of the work described in the manuscript, i.e., what was studied with what methods and what were the main results, and Conclusions should contain summary of the results and their significance. At the moment they do not do this. More precisely, currently Abstract is missing many of these details and Conclusions feels more like an extension of Discussion. I suggest significantly improving the current presentation.

We have modified Abstract and Conclusions accordingly

In the Abstract you talk about identified compounds, although there were no single compound really identified in the whole study. This should be changed.

Referee #1 has raised a similar comment. We agree and modified the sentence to:

We report the molecular formulas of the HOMs and show the differences in the oxidation patterns of these ArHCs.

In the Abstract you talk about mechanistic pathways – was there more than the one shown for mesitylene in Figure 6?

We show a possible oxidation pathway for mesitylene as an example case. The other single ring aromatics may follow a similar scheme, although branching ratios may vary. We now say:

A potential pathway for the formation of these HOMs from aromatics is presented and discussed.

Also in line 53 you say that you talk about "potential pathways and possible mechanism", but I feel that currently the mechanistic aspects are only briefly discussed.

Indeed, the lack of unambiguous identification of molecular structures does not allow for an extensive evaluation of the mechanism. We present a generalized scheme of a mechanism, which represents the observed elemental composition of species, and discuss a potential pathway of HOMs formation. We changed the wording such that it should be clear that we do not provide proofs of a detailed mechanism. The sentence reads now:

Here we show the formation of HOMs from ArHC upon reaction with OH radicals. We present product distributions of HOMs in terms of molecular masses and molecular formulas for a series of

aromatic precursors based on measurements with a nitrate chemical ionization atmospheric pressure interface time of flight mass spectrometer (CI-APi-TOF) (Ehn et al., 2014; Jokinen et al., 2012; Kürten et al., 2011). A potential pathway along with a possible mechanism for the formation of HOMs from aromatic compounds is discussed.

More details of the OH radical production, especially the geometry and the distance OH needs to travel, could be helpful. It was stated that this setup has been used to generate HO₂, which is co-produced by H₂O photolysis in presence of O₂, but HO₂ is much less reactive and thus can travel much further, whereas OH is easily lost to impurities and walls (and as far as I understood OH needs to travel through two 90 degree bends, from which at least the other is a turbulent zone?). Was there only one experiment with one hydrocarbon?

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 entering the mixing zone are OH, HO₂, O₃ and H₂O₂. Their concentrations depend on the residence time in the lamp and the reaction time in the transfer region. This is now explained in Appendix C together with the chemical reactions forming the oxidants. Despite potentially higher losses of OH to the walls compared to HO₂, there was still enough OH present to react with the precursor gases. The same setup was used for all precursors and for D9-butanol. From this we derived an initial OH concentration of about $8.5 \cdot 10^{11} \text{ cm}^{-3}$.

See Appendix C.

Was the OH production always exactly the same? These should be stated clearly.

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 $2 \cdot 10^8$ 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.

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 $2 \cdot 10^8$ 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.

It would be very helpful to give the precursor structures to help the reader understand the significance of these oxidation processes.

The chemical structures of the precursors are now included in Figure 2.

Line 84: Could you include a figure showing the process of OH concentration determination as it is very central to the whole topic.

An average OH concentration was determined from the decrease of the precursor gases with the lamp off and on. Using a kinetic model we derived the initial OH concentration and the profile of the precursors. This is now provided in Appendix C.

Line 86: You talk about reactive non-aromatic double bonds together with 140 ppbv ozone – how is it “expected” that O₃ reactions do not play a role here?

This question was also raised by referee #1.

While the ArHC do not react with ozone, oxidation products with remaining double bonds indeed do. 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 $10^{16} - 10^{18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 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.

Line 112: Would you expect the dimer/monomer ratio to be constant? If, then why so? This should be stated. Furthermore, what do you mean by this being a good proxy? How and why?

We do not expect the dimer to monomer ratio to be the same for all precursors. Indeed the ratios might be somewhat different when measured with different instruments because the transmission functions are not the same. Since the transmission of ions may vary with the voltage settings in the two quadrupoles in the APi, dimer:monomer ratios may differ between instruments. However, since the transmission curve is expected to be rather smooth the relative trend of the dimer/monomer within the 5 single-ring ArHC may still be reasonably accurate due to the small mass differences in the monomer and dimer ranges. We modified the sentence:

However, since the mass-dependent ion transmission efficiency is rather smooth the given values may faithfully represent the relative behavior of the product distribution of the different aromatic compounds.

Line 117: How much of the given abundancies could be actually due to shifting transmission of the mass spec? Is this a potential problem?

As commented above this should have a small effect on the relative changes of the monomer:dimer ratio. This could be a problem if the instrument were tuned in such a way that the ion transmission is strongly mass dependent. Usually, one tries to avoid this.

Line 118: I guess this also assumes that the $k(\text{RO}_2 + \text{HO}_2)$ is similar for all systems? Should be stated. Moreover, according to Table 1 different VOC concentrations were used (which have different rate coefficients with OH), which leads to different $[\text{RO}_2]$ and to different strength of $\text{RO}_2 + \text{RO}_2$, right?

Yes, we assume a similar $k(\text{RO}_2 + \text{HO}_2)$. We think it is a reasonable assumption that the reaction rate $\text{RO}_2 + \text{HO}_2$ does vary less with different substituents compared to the reaction of RO_2 with RO_2 . The master chemical mechanism also uses just one rate constant for this reaction.

The lamp produces a similar concentration of OH and HO_2 in all experiments independent of the precursor concentration. This means that the concentration of RO_2 produced and the amount of HO_2 present is similar in the different experiments. In our sensitivity test with the flow tube kinetic model for mesitylene we selected the species TM135BPOOH and TM135BP2OH as proxy for products of $\text{RO}_2\text{-HO}_2$ and $\text{RO}_2\text{-RO}_2$ reactions. When the initial mesitylene concentration and the reaction rate coefficient with the OH radical were doubled the ratio TM135BPOOH / TM135BP2OH changed only by 18%. Therefore we believe that the observed differences among the tested ArHC compounds can be attributed to a different selectivity rather than to a different radical concentration. We changed the text to:

This indicates that the branching ratio of $\text{RO}_2 + \text{RO}_2$ to dimer (R3c) compared to the other reaction channels (R3a,b) is higher for the more substituted aromatics. This is based on the assumption that the lamp produces similar concentrations of OH and HO_2 radicals and that the reaction rate coefficients $k(\text{RO}_2 + \text{HO}_2)$ (R4a) are similar for all RO_2 .

Line 127: You should clearly separate speculation, i.e., do you know if the stated radicals are forming observed dimers?

We agree, we replaced the text with:

Furthermore, we assume that less oxygenated radicals, although not quantitatively detected by the CI-APi-TOF (Berndt et al., 2015; Hyttinen et al., 2015), will nevertheless participate in the dimer formation.

Lines 145 to 174: In talking about products which main difference is the amount of O-atoms, it seems a bit confusing that all of them have the same label “z”. Could you think of any other way of representing them so that it would not seem they all have the same “z-amount” of O-atoms.

We consider “z” as a variable which can be any number while we focus on the hydrogen atom number. To make it more explicit we added:

Where z denotes any number of oxygen atoms,

Line 174: Does this formula mean that you found products with 4 and 6 H-atoms more than in the parent VOC?. How could you get to a product with 6 H-atoms more than in the parent structure?

Can you give an example how this could happen?

HOMs with 6 hydrogen atoms more were in general a very small fraction of the total detected HOMs signal (this is true for the dimers as well). As an example one could think that the first OH adds one hydrogen atom to the initial ArHC and the termination of the radical chain to an alcohol or hydroperoxy function adds a second hydrogen atom. If the remaining 2 double bonds are not cleaved within the radical chain propagation this mechanism can be repeated up to 3 times, each time adding 2 hydrogen atoms. This can indeed lead to HOMs with 6 hydrogen atoms more than the ArHC precursor. This was already described in lines 194-197.

Line 181: What do you mean by “lower than expected H-atom number”?

We mean less hydrogen atoms than the precursor. We write now:

Similarly, the compounds with an H-atom number lower than the ArHC precursor could have been formed by an H-abstraction from first generation products with formula $C_xH_yO_z$.

Line 192: What do you mean by “much less H-atoms than terpenes”?

We mean that the fragmentation could involve the elimination of a fragment that contains hydrogen atoms instead of CO alone.

HOMs with less C atoms than the parent molecule have also been previously described from terpene precursors via CO elimination (Rissanen et al., 2014, 2015). Here, the aromatics show mostly also a loss of H-atoms when fragmenting. This indicates that a methyl group can be lost after oxidation to an alkoxy radical as formaldehyde or a carbon fragment can be lost after ring cleavage.

Line 192: Methyl group is not generally considered a good leaving group. Could you add a brief explanation or a reference?

If an H-atom is abstracted from a methyl group an alkoxy radical can be formed, which can decompose with the loss of H_2CO . See corrected text above.

Line 194: The occurrence of multiple OH attacks seems somewhat obvious from the observed product compositions. However, the given OH concentration together with such a short residence time in the flow tube does not seem to allow much 2nd generation oxidation (and of course even less 3rd generation). I think this fact should be addressed in the text. Perhaps a chemical reaction simulation could help to get an idea of the needed RO₂ lifetimes and the OH + product reaction rates to justify the high amounts of products evident from figures. Actually, the figures seem to indicate way higher product concentrations than what was the used reagent concentration ($=[OH]$). For example, Figure 3 gives a concentration of $>3 \times 10^9 \text{ cm}^{-3}$ for a single product, even though the stated $[OH]$ was only $2 \times 10^8 \text{ cm}^{-3}$ which should equal to the maximum product concentration, right?

The reported OH radical concentration is an average value. Due to the fast reaction the OH radical concentration is much higher at the beginning of the flow tube. Initial OH levels are about $8.5 \times 10^{11} \text{ cm}^{-3}$ and rapidly drop off a few orders of magnitude. Up to 23% of the precursor gas reacts and

therefore an OH attack on the first generation products can occur in such a short reaction time. We report the modeled OH radical concentration in the Appendix C.

Line 201: What do you mean by “conjugated radical in an allylic position”? This should be rewritten.

We rephrased the whole sentence, see reply to comment on line 229 below

Line 205: What do you mean by “This mechanism varies among the ArHC tested.”? How is the mechanism changing?

We delete this sentence. Variations in the mechanism are provided just thereafter in the text.

Line 211: A reference should be added for: “termination reactions of alkoxy radicals make double bonds”. Is that a possible reaction for alkoxy radicals?

The manuscript is not correctly cited. We say that when the radical chain is interrupted the molecule can still have double bonds which are reactive sites towards OH radical attack.

Line 229: Oxygen bridged bicyclic radicals were not discussed in the text.

This was shown in line 204 and Figure 6. We rephrased it as follows:

After addition of OH and loss of aromaticity an oxygen molecule can be added forming a peroxy radical. It has been established that the latter can cyclize producing a second stabilized allylic radical with an endocyclic O₂ bridge (Baltaretu et al., 2009; Birdsall and Elrod, 2011; Pan and Wang, 2014). On this oxygen bridged bicyclic radical further oxygen addition and cyclization might occur up to a peroxy radical with seven oxygen atoms (C₉H₁₃O₇), which is the species detected at relatively high intensity (3.5%).

Line 230: The oxygen addition to allylic positions was not really discussed in the text.

It is now mentioned, see above.

Line 236: There was no discussion about phenolic structures in the main text. As already stated above, the current conclusions would rather fit as a continuation of discussion and not as a “conclusions” chapter.

We agree with the referee, we move this part to the results and discussion section and rephrased it:

Recent studies (Nakao et al., 2011; Schwantes et al., 2017) suggest a mechanism where the initial step is the formation of the phenolic equivalent ArHC followed by additional oxidation steps yielding “polyphenolic” structures with high O:C ratio (up to 1.2). However literature data are showing varying yields for the conversion of arenes to phenols via the OH radical addition and H elimination. According to MCM 3.3.1 (Jenkin et al., 2003) benzene and toluene have quite high phenol yields (approximately 50 and 20 %, respectively) while mesitylene shows a rather small yield (4%). This fact should be reflected in the final HOMs yield with alkyl substituted ArHCs being less effective in yielding HOMs. However in our experiments we did not detect such a difference in the HOMs yields linked to phenol formation yields. A relevant fraction of the detected HOMs showed a hydrogen atom number higher than the precursor ArHC which cannot be explained with the presence of just polyphenolic compounds as oxidation products.

Line 245: Please rewrite sentence starting with “Furthermore..”.

We replaced it with:

Furthermore, the fact that the oxidation of ArHC can rapidly form HOMs of very low volatility makes ArHC a potential contributor to nucleation and early particle growth during nucleation episodes observed in urban areas.

Figure 1: Excimer.

We corrected eximer with excimer.

Figure 2: I wonder what was your calibration procedure for the mass spectrometer?

The HOMs quantification is based on the calibration factor for sulfuric acid ($6.5 \cdot 10^9 \text{ cm}^{-3}$) 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. No further characterization of the system CIMS - ArHC HOMs was pursued.

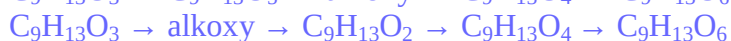
Figure 4 caption: What do you mean by “ethylbenzene does not follow this empirical observation”? What is the empirical observation, and how ethylbenzene does not follow it?

With empirical observation we want to indicate the fact that with the increase of the number of the substituents less HOMs species are needed to sum up to the 80% of the total HOMs signal. While this is true for the series benzene, toluene, xylene, mesitylene, ethylbenzene deviates from this trend. This text now reads:

However, this trend with the increase of the number of substituents is not met by ethylbenzene

Figure 5: This figure needs some improvement: How do you go from $\text{C}_9\text{H}_{13}\text{O}_3$ through alkoxy radical to $\text{C}_9\text{H}_{13}\text{O}_6$? Also, you say that yellow box contains even oxygen species, even though it has also odd oxygen species.

The scheme is a simplified representation of the HOMs formation for mesitylene. We made two changes to the Figure: 1) The alkoxy radical chain is now in a separate box and 2) we added $\text{C}_9\text{H}_{13}\text{O}_4$ to the alkoxy radicals. The arrow links now the odd-oxygen radical box with the alkoxy (even oxygen number) box, from which then the even-oxygen radicals can be produced. The formation of the alkoxy radical can occur from any odd-oxygen peroxy radical. For example $\text{C}_9\text{H}_{13}\text{O}_6$ can be formed via two pathways:



We replace line 490 with:

Radicals in the orange box are from the propagation of the initial OH attack with an odd number of oxygen atoms, radicals in the pink box are formed via an alkoxy intermediate step with an even number of oxygen atoms, while radicals in the purple box are products of a second OH addition.

Table A-1: You talk about species losing methyl groups in the text, but what explains the benzene products with less C-atoms than the parent?

In the text we explained how a methyl group can be oxidized and become a good leaving group (e.g. formaldehyde). This is not possible for benzene. However if the autoxidation leads to a ring opening step the resulting radicals can undergo carbon chain fragmentation yielding small fragments (e.g. carbon monoxide, glyoxal).

Minor Comments:

Line 35: I don't think CCN (anymore) exert an influence on pre-industrial times (i.e., be careful with the wording).

We agree and changed the wording to:

CCN can impact climate via their influence on cloud properties; this changes the radiation balance nowadays and did even more so in the pre-industrial period (Carslaw et al., 2013; Gordon et al., 2016).

Line 44: I guess it's really hard to prove that something does not happen, right? So I'm a bit wondering why so many references have been grouped to indicate that no HOMs were seen by studies that did not use the current methods able to detect the HOMs in the first place.

We rewrote this to read:

Despite the fact that ArHC·OH adducts under atmospheric conditions react with O₂ to yield peroxy radicals (Calvert et al., 2002; Glowacki et al., 2009; Suh et al., 2003) it is not known if ArHC oxidation also yields HOMs. No carbon balance could be reached so far and generally only about 50% of the carbon reacted was identified as products (Calvert et al., 2002). When aromaticity is lost by the OH addition non-aromatic double bonds are formed representing highly reactive products to more oxidants, which is a peculiar behavior not observed in other classes of VOC (Calvert et al., 2002).

Line 49: Multiple non-aromatic double bonds exists also in many terpenoid species, so it's wrong to argue that this is a property of aromatics alone.

Here we want to say that if ArHC loose their aromaticity products can also become reactive towards other oxidants like O₃ and NO₃ (Calvert et al., 2002). We now point this out in the previous answer.

Line 67: I think it could help the reader if you could provide a bit more details about OH generation. At least I cannot fully understand the method how it's described now. Do you have an injector or why is the coaxial geometry mentioned?

More information is now provided in Appendix C. We mention the coaxial geometry because coaxial is the geometry of the excimer lamp we used for this series of experiments.

Line 79: "acid-base reaction" – do you mean salt formation?

We mean the abstraction of an acidic H-atom from the HOM by NO₃⁻, see reaction R2.

Line 96: The stated "monomer" and "dimer" ranges overlap.

Yes, since we studied ArHc with increasing molar mass it is not possible to give an unequivocal range for monomers and dimers for all species.

Line 99: Which one is 14 Th – methyl or ethyl group. . .?

An H-atom is replaced by a methyl group: Methyl (CH₃(15 Th) – H(1 Th)). In case of ethylbenzene a CH₂ group is added compared to toluene. We changed the sentence to:

...is shifted by differences of 14 Th (CH₂) each from benzene via toluene and xylene/ethylbenzene to mesitylene due to the additional substituent groups

Line 107: What "a mechanism for Van der Waals interactions.." means? Is there a "mechanism"?

We replaced this with:

Most of the higher n-mers are probably bonded by intermolecular interactions, similar to biogenic HOMs (Donahue et al., 2013).

Line 108: I don't understand why would you talk about 800 Th cluster as a particle while talking about mass spectrometric results? Could you explain the significance of adding this here?

We made this link because clusters of this size can already be detected by particle counters. Thus mass spectrometry and particle measurements start to overlap and mass spectrometry can help to identify which compounds are participating in NPF. We modified the sentence:

Clusters with m/z ≥ 800 Th might already be detected by particle counters with a mobility diameter d ≥ 1.5 nm

Line 121: I wonder if a “monocyclic dimer” is a correct term here, if you do not know if the ring is retained in the reaction or not. Maybe better to reword to state that it is a “dimer” that was generated by monocyclic ArHC.

We agree and replaced this with:

while dimers that were generated from monocyclic ArHC have on average

Line 125: What is an “auto-termination reaction”?

It is an intramolecular decomposition that leads to a non-radical organic species and an OH radical as an example. We assessed a similar question from referee #1, to now read:

Additionally, more oxygenated radicals have a higher probability to undergo a unimolecular termination compared to a radical-radical recombination ($\text{RO}_2\cdot + \text{RO}_2\cdot$ 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 group which results in an OH radical loss and a carbonyl group formation. Therefore, the fraction of dimer formation should decrease with higher oxygen content.

Line 125: Where is the comparison between unimolecular and bimolecular channels based on?

As explained before, more oxygen atoms in the HOM imply more peroxide functional groups which increases the probability of the unimolecular pathway. This decreases the fraction of dimers with increasing oxygen content.

Line 128: What is a “higher-order cluster”?

With higher-order cluster we indicate n-mers where the precursor monomeric structure appears 3 or more times. While in the text we refer to them as trimers, tetramers and pentamers when the monomer structure appears 3, 4 and 5 times, respectively, we want to clarify that if monomers and dimers are produced via radical unimolecular termination or the radical-radical reactions reported in the text (R3a-c and R4a,b) higher order clusters (trimers, tetramers, pentamers) are most likely resulting from the aggregation of these monomer and dimer HOMs via the establishment of van der Waals interactions.

Line 134: add -s to “pathway”.

We replaced this with:

The increasing number of methyl groups appears to influence the oxidation pathways and leads to less HOM products.

Line 150: Both products have same number of O-atoms (=z).

We corrected the chemical formulas.

Line 153: Rather odd number of H-atoms?

In case of an OH addition an O-atom is added followed by O_2 additions, which leads to an odd number of oxygen atoms (z_o). In case of an H-atom abstraction O_2 adds to the carbon radical and further autoxidation would then produce an even number of oxygen atoms (z_e).

Line 157: Is Hyttinen 2015 the right reference for this?

Yes, it is.

Line 162: I don't think Kirkby 2016 is generally a good reference for peroxy radical mechanisms as it seems to contain all the mechanistic aspects in its supplementary material.

We removed Kirkby 2016 as a reference here.

Line 166: Also reaction 4b forms RO radicals.

We replaced this with:

These alkoxy radicals (R3a, R4b) may isomerize to an alcohol by internal H-abstraction forming a carbon centered radical.

Line 167: Oxygen molecule.

We replaced atom with molecule.

Line 169: What do you mean by “discrepancy between the intensity of the peaks”?

We find a prevalence of monomers with formulae $C_xH_{y+2}O_z$ compared to those with formulae $C_xH_yO_z$. On average reaction R3b should yield similar concentrations. From the flow tube kinetic model in Appendix C we note that the HO_2 radical concentration is very high during the whole experiment because it is also formed in the source. From this we infer that the radical termination reaction R4a is the main sink of the peroxyradicals under these specific conditions of our experiments .

We say now:

The much higher intensity of the peaks with formula $C_xH_{y+2}O_z$ compared to those with the composition $C_xH_yO_z$ can be ascribed to a high contribution from the recombination of $RO_2\cdot$ with $HO_2\cdot$ (R4a). This is due to the high HO_2 concentration in our experiments since HO_2 is also formed in the OH radical source.

Line 196: For which compounds the third OH attack is seen?

Benzene, ethylbenzene, xylene, naphthalene and biphenyl show HOMs that can be linked to a third OH attack. The contribution of these HOMs to the total of the detected signals is however always extremely low.

A third OH attack is observed only for some compounds: benzene, ethylbenzene, xylene, naphthalene and biphenyl; the contribution of these HOMs to the total of the detected signals is always extremely low. The mechanism will likely proceed in a similar way.

Line 211: Should be Kurten 2015?

The referee is right, we wanted to refer here to: Kurtén, T., Rissanen, M. P., Mackeprang, K., Thornton, J. A., Hyttinen, N., Jørgensen, S., Ehn, M. and Kjaergaard, H. G.: Computational study of hydrogen shifts and ring-opening mechanisms in α -pinene ozonolysis products, J. Phys. Chem. A, 119(46), 11366–11375, doi:10.1021/acs.jpca.5b08948, 2015.

Line 218: Too less C atoms in biphenyl dimer.

This was indeed a typo. We replaced with:

$C_{24}H_{22}O_8$.

Line 219: Aromatic rings are generally considered rather unreactive than reactive.

We wanted to say that the remaining aromatic ring is still quite reactive towards a second attack by OH radicals. We now say:

Compounds with extra-high H-atoms are more frequently found for biphenyl, which is expected as there is a second reactive aromatic ring remaining after (auto)-oxidation of the first one.

Line 234: Should be “and” not “or”.

We agree and changed this to and.

Line 467: Should be “due” not “doe”.

done

Table 1 caption: Why do you state “mixing ratio” here?

We replaced it with concentration.

Table 2: Would it make more sense to express the fraction in percentage so that the O:C and the fractional part would not be mixed so easily?

Good suggestion. We express now monomer and dimer fractions in percentage.

Figure 3 caption: There are no compositions in the given inserts, although they're mentioned. Can the mass spec really retrieve accurate compositions for the pentamers?

This class of mass spectrometer shows a resolution of 4-5000 with a flattening above mass 150-200 Th. Such resolution is certainly insufficient alone when it comes to provide a peak chemical composition at high masses. However, during the peak analysis process it is possible to infer the chemical composition of the peaks present in the mass spectra, taking advantage of the following assumptions:

- the elements possibly present are carbon, hydrogen; oxygen and nitrogen as a nitrate ion,
- the ratio between these elements has to allow a reasonable chemical structure (e.g. unsaturation number),
- the precursor carbon chain gives some constraints on the number of carbon atoms expected in the chemical formula with no fragmentation due to the ionization process because of the soft ionization method,
- the peak distribution can suggest a repetition of building blocks (e.g. monomer, dimer, trimer, tetramer) as well as peak compositions that differ by 2 hydrogen atoms (2.0157 amu) or 1 oxygen atom (15.9949 amu),

We do not report the chemical composition in the insert, however, all the peaks plotted here are identified with their chemical composition. Pentamers from biphenyl were identified up to mass 1242.3307 Th corresponding to the chemical formula $C_{60}H_{60}O_{25}(NO_3)^-$.

Line 242: I'm not sure if you should talk about identification here, rather "have curiously the same compositions as..". In addition I think also this part should be in Discussion section.

We agree. We now close the manuscript with a paragraph "Discussion and atmospheric implications" and we replaced the text with:

Some of the HOMs measured here from the oxidation of ArHC have the same composition as the HOMs formulae identified by Bianchi et al. (2016) during winter time nucleation episodes at the Jungfraujoch High Altitude Research Station.

Appendix B: Figures of the parent compounds also here would make the figures more interesting.

We included the ArHC structures in each figure.

References

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