

## 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)

1.92: If you present molar yields, you must have information about the sensitivity of your mass spectrometer. In addition the y-axis in Figures 2 and 3 seem to be given in molecule concentration. (If not, that should be clarified in the captions.) At C1 other parts of the manuscript you mention that you cannot quantify dimers because the transmission of your TOF-MS is unknown. In this manuscript, any information about the sensitivity of your instrument is missing. How did you estimate the molar yields then? Please, state precisely in the experimental section, what you did to determine the sensitivity or what the basis of your assumptions is.

We answered this point in our reply to referee #1. The HOM molar yield was calculated from the ratio of HOM concentration to reacted ArHC (the yields were not corrected for HOMs losses in the flow tube). The amount of ArHC reacted was calculated based on the assumption that the OH production was similar in all experiments. The OH concentration was determined from the difference in precursor concentration between excimer lamp switched on or off from two D9-butanol, toluene, mesitylene, and biphenyl experiments. 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. No further characterization of the system CIMS - ArHC HOMs was pursued. 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  $2 \cdot 10^8 \text{ OH cm}^{-3}$  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

Initial concentrations of precursors, reaction rate coefficients, ArHC reacted fraction (%), total HOMs concentration and HOMs yield (%) relative to the reacted ArHC. The mixing ratio of precursors was determined at the exit of the flow tube when the excimer lamp (OH generation) was switched off.

| Compound                           | Concentration<br>(molecules $\text{cm}^{-3}$ ) | $k_{\text{OH}}$<br>( $10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) | Reacted fraction<br>(%) | [HOM]<br>(molecules $\text{cm}^{-3}$ ) | HOMs yield<br>(%) |
|------------------------------------|--|--|-------------------------|--|-------------------|
| Benzene ( $\text{C}_6\text{H}_6$ ) | $9.85 \cdot 10^{13}$                           | 1.22   | 0.5                     | $1.2 \cdot 10^9$                       | 0.2               |
| Toluene ( $\text{C}_7\text{H}_8$ ) | $1.97 \cdot 10^{13}$                           | 5.63   | 2.3                     | $4.4 \cdot 10^8$                       | 0.1               |

|   |                       |                |      |                      |     |
|---|-----------------------|----------------|------|----------------------|-----|
| Ethylbenzene<br>(C <sub>8</sub> H <sub>10</sub> )   | 1.13 10 <sup>13</sup> | 7.0            | 2.8  | 9.4 10 <sup>8</sup>  | 0.3 |
| (o/m/p)-xylene<br>(C <sub>8</sub> H <sub>10</sub> ) | 2.95 10 <sup>12</sup> | 13.6/23.1/14.3 | //   | 2.8 10 <sup>9</sup>  | //  |
| Mesitylene<br>(C <sub>9</sub> H <sub>12</sub> )     | 2.46 10 <sup>12</sup> | 56.7           | 22.7 | 3.1 10 <sup>9</sup>  | 0.6 |
| Naphthalene<br>(C <sub>10</sub> H <sub>8</sub> )    | 2.95 10 <sup>13</sup> | 23.0           | 9.2  | 1.4 10 <sup>10</sup> | 0.5 |
| Biphenyl<br>(C <sub>12</sub> H <sub>10</sub> )      | 4.43 10 <sup>13</sup> | 7.1            | 2.8  | 1.8 10 <sup>10</sup> | 1.4 |

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

p4, l.119: Does the split off of O<sub>2</sub> explain the lower oxidation degrees of dimers assuming RO<sub>2</sub>+RO<sub>2</sub> = ROOR +O<sub>2</sub> or not?

We think this could be an explanation. We already give this explanation in line 122ff. To corroborate it we would need dedicated experiments which are beyond the scope of this paper.

p.4, l.119f and p.6, l.162: I would propose to give here Mentel et al. 2015 somewhat more recognition as they described, based on experimental observations in context of autoxidation, this type of dimer formation including mixed dimers a year before Kirkby et al. 2016. The same is true for the alkoxy path.

We added Mentel et al., (2015) instead of Kirkby et al. (2016) in the citations given in line 124 and line 162.

p.4, l.192ff: “Additionally, more oxygenated radicals have a higher probability to undergo an auto-termination radical reaction compared to a radical-radical recombination (RO<sub>2</sub>· + RO<sub>2</sub>· or RO<sub>2</sub>· + HO<sub>2</sub>·).” I don’t exactly what you want to say with this statement in context of degree of methylation and dimer fraction. Less methylated aromatic compounds tend to more auto-termination? What means auto-termination - termination by internal reaction?

The referee seems to address our statement in line 124. Similar questions were also raised by referee #2. We report here our answer.

This statement can be derived from Rissanen 2014: We rewrote it:

Additionally, more oxygenated radicals have a higher probability to undergo a unimolecular termination compared to a radical-radical recombination (RO<sub>2</sub>· + RO<sub>2</sub>· or RO<sub>2</sub>· + HO<sub>2</sub>·. 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.

p.8, l231ff: I think, that one should differentiate clearer between autoxidation by H-shift to peroxy radicals on one hand and by attack of the peroxy moiety to internal double bonds on the other hand. Although both reactions are internal rearrangements they are still of different character, as the first needs “mobile” H-atoms and the latter double bonds with potential to allyl radical formation. As a consequence the HOM formation in aromatic systems would be based - at least in parts- on a different mechanism?!

We agree with the referee. We rewrote this to read:

The autoxidation radical chain reaction is thought to proceed via intra-molecular abstraction of a hydrogen atom from an acidic C-H bond by a peroxy radical and the consequent formation of a

hydroperoxy functional group and a carbon centered radical that can take up an oxygen molecule from the surrounding and eventually repeat the whole process n times (here called Type I autoxidation). In the case of aromatic compounds, when the aromaticity is destroyed, Type II autoxidation may happen by further addition of oxygen to the allylic resonance-stabilized radical followed by an attack of the peroxy group to the internal double bonds forming an oxygen bridge. This can proceed up to a peroxy radical of 7 oxygen. We speculate that Type II autoxidation might also occur in organic molecules with two double bonds like isoprene and limonene.

p.4, l.96 Thomson

Done

p.7, l.218; “strongest dimer is C<sub>12</sub>H<sub>14</sub>O<sub>8</sub> for benzene and C<sub>12</sub>H<sub>22</sub>O<sub>8</sub> for biphenyl, respectively”. I guess a typo, as C<sub>12</sub>H<sub>22</sub>O<sub>8</sub> cannot be a dimer resulting from biphenyl.

Yes this was a typo. We replaced it with C<sub>24</sub>H<sub>22</sub>O<sub>8</sub>.

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