

We thank the reviewers for going through our manuscript titled “*An aldehyde as a rapid source of secondary aerosol precursors: Theoretical and experimental study of hexanal autoxidation*” and for their constructive suggestions on how to improve the work. We have incorporated all the suggestion and have modified the revised manuscript accordingly. Below, the reviewer queries are reproduced in red, followed by detailed point-by-point author responses in blue, and the changes and additions to the revised manuscript and the supplement in purple.

Referee #2 (report #2)

The revision addressed most of my earlier concerns. I appreciate that the authors performed additional experiments to verify a few questions. I have just two additional questions regarding their responses.

1. The authors uphold their interpretation of the C₆H₁₁O₆ peak in 1.4 s reaction time, as from C₆H₁₁O₅-RO₂ + RO₂ to form C₆H₁₁O₄-RO and this RO isomerizes to form C₆H₁₁O₆. How fast is this RO isomerization to compete with O₂ addition and RO decomposition? If the authors’ interpretation is true, then why were there no other products from RO₂ + RO₂ (i.e., C₆H₁₂O₅ alcohol, which has two O-H bonds). For typical RO₂ + RO₂ reactions, especially for secondary RO₂ as shown in Figure 4, the following reactions are expected to take place at the same time (different branching ratios, but both are major pathways):



For that secondary C₆H₁₁O₅-RO₂, the branching ratio to form RO is expected to be ~ 0.6 and the R-OH + R=O to be ~0.4. Some RO may add oxygen to form R=O again and some RO₂ may decompose. Thus, I would expect that the C₆H₁₁O₆-RO₂ have similar abundance as C₆H₁₀O₅+C₆H₁₂O₅. Although C₆H₁₀O₅ may not have great sensitivity, the C₆H₁₂O₅ product should be present in the mass spectrum. Here, what I cannot understand is that the author suggest that reaction (2) is dominant in as short as 1.4 s, but no evidence of reaction (1) was observed in 1.4 s. Why so?

In addition, in their response, the authors claimed that reaction (1) is not important because their observation didn’t show similar R-OH and R=O intensities. Isn’t this self-contradicting? Or why do the authors think reaction (2) is important, but reaction (1) is not under the same RO₂/HO₂ condition for the same reacting RO₂?

Response: First, we acknowledge the fact that the secondary C₆H₁₁O₅-RO₂ can undergo both reactions (1) and (2). The C₆H₁₁O₅-RO₂ radical undergoing reaction (1) can form less oxygenated closed-shell products C₆H₁₀O₄ (i.e., R=O) and C₆H₁₂O₄ (R-OH) but not C₆H₁₀O₅+C₆H₁₂O₅ as the reviewer pointed. Despite the two H-bonding groups, the target molecule (C₆H₁₂O₄) with 4 oxygen atoms is likely too weakly bound to NO₃⁻ to be detected. (Hyttinen et al. *J. Phys. Chem. A* **2018**, 122, 269–279). In Hyttinen et al. (2018), they show that, for their model systems with two hydrogen bonding functional groups, molecules with 4 oxygen atoms have a binding energy with NO₃⁻ that is weaker than that of the nitrate dimer

($\text{HNO}_3 \cdot \text{NO}_3^-$). As a consequence, the NO_3 -CIMS has a low sensitivity for the 4 oxygen containing molecule ($\text{C}_6\text{H}_{12}\text{O}_4$).

On the other hand, the $\text{C}_6\text{H}_{11}\text{O}_5\text{-RO}_2$ undergoing reaction (2) can produce a reactive RO with which can follow isomerization reaction (in competition with $\text{RO} + \text{O}_2$, and RO decomposition reactions) which is the key to form the dominant $\text{C}_6\text{H}_{11}\text{O}_6\text{-RO}_2$ (an alkyl peroxy radical with even number of oxygen atoms originated from hexanal OH oxidation) observed experimentally. Based on our current understanding, an alkoxy radical with five (or more) carbon atoms will be more prone isomerization than fragmentation.

Now, unlike the secondary $\text{C}_6\text{H}_{11}\text{O}_5\text{-RO}_2$ undergoing one bimolecular step ($\text{RO}_2 + \text{RO}_2$), we would not expect the dominant $\text{C}_6\text{H}_{11}\text{O}_6\text{-RO}_2$ undergo a second bimolecular reaction within 1.4 s. This is likely the reason we do not see the evidence of reaction (1) for $\text{C}_6\text{H}_{11}\text{O}_6\text{-RO}_2$ yielding $\text{C}_6\text{H}_{10}\text{O}_5 + \text{C}_6\text{H}_{12}\text{O}_5$ within 1.4 s reaction time.

In connection to the previous response, where the reaction (1) was initially given somewhat less importance (although latter acknowledged in the revised manuscript) while explaining the distribution of the closed-shell $\text{C}_6\text{H}_{10}\text{O}_5$ and $\text{C}_6\text{H}_{12}\text{O}_5$ products in the higher residence time experiments, we agree that the reactions (1) and (2) take place at same time. We thank to the reviewer to point out the branching ratios of reactions (1) and (2).

2. In Figure S1, the chemical formulas of the major peaks should be labeled.

Response: The mass spectral peaks in Figure S1 are not identified which we refer as background signals (mainly originating from the zero-air source) and the background spectra are subtracted accordingly from the hexanal OH oxidation spectrum as mentioned in the main manuscript.

Referee #3 (report #1)

The authors did a great and thorough job in addressing all reviewers comments. However, there is an aspect that I would like to see clarified with more detail, and it is related to the fact that the authors only find one TS conformer for the aldehydic H-abstraction. I performed a very quick search at the M08-HX/pcseg-2 level and found 5 unique aldehydic TS conformers, all within 1 kcal/mol. I would suggest that the authors take the Cartesian coordinates that I am providing, reoptimize these structures at their chosen level of theory and verify if they obtain more TSs than the one that they already have. If they do, what is the effect of including them on the rate constant?

The Cartesian coordinates:

```
O -3.5157423078 -0.7705013644 0.1908610098
C 0.7295103392 0.2362464807 0.0888256259
C -0.7031565879 -0.2837666536 0.0508583823
C 1.7640772110 -0.8618431621 -0.1346671071
C -1.7212591969 0.8330119581 0.2192926397
C 3.1928290922 -0.3327974852 -0.0768257030
C -3.1505390214 0.3610514630 0.2295652609
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H -1.5702141044 1.3852218175 1.1574736605
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H -5.6069971016 2.1937664316 -0.0999879850

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O -4.2459618367 0.2142833881 1.0732261213
C 0.4283235015 0.2432090007 -0.0620283067
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H -4.1756937406 -0.9110694557 -2.4911863982

Response: We thank the reviewer for the additional TS conformer geometries for the OH aldehydic H-abstraction. We reoptimized them at the MN15/def2-tzvp level of theory and found two new TS conformers, one of which is the global minima aldehydic H-abstraction TS conformer, lower than what we reported previously. Of the remaining 3 conformers, one was a duplicate and the other two did not optimize to transition states. Including the two additional TS conformers along with the original TS conformer in the bimolecular MC-TST equation gives us a low aldehydic H-abstraction rate coefficient (8.57×10^{-13}). While this is slightly faster than our previous MC-TST rate coefficient (4.14×10^{-13}), it is still significantly slower than the literature experimental value. The significantly higher number of reactant hexanal conformers likely has a large influence on this slow rate. However, the new TS conformer leads to a perceptible increase in our lowest conformer TST (LC-TST) rate coefficient. We now provide the new LC-TST rate coefficient and the corresponding branching ratios in the main manuscript (Table 1), and provide both LC-TST and MC-TST rate coefficients in the *Supplementary Table S2*.

Changes to manuscript: In Table 1, we updated the aldehydic H-abstraction rate coefficient, branching ratios and the overall rate coefficient.

Changes to supplement: In Supplementary Table S2, we updated the LC-TST and MC-TST aldehydic H-abstraction rate coefficients.