

# ***Interactive comment on “Highly oxygenated organic molecules (HOM) formation in the isoprene oxidation by NO<sub>3</sub> radical” by Defeng Zhao et al.***

## **Anonymous Referee #3**

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### General Comments

This study identifies important HOMs (highly oxygenated organic molecules) from isoprene + NO<sub>3</sub> reaction through chamber experiments. The identification of HOMs from NO<sub>3</sub> oxidation have been less studied than those from OH or O<sub>3</sub> oxidation, so this study fills an important gap in atmospheric chemistry. This study uniquely and in great detail connects many measured compounds to possible mechanistic formation pathways. I suggest this paper be published with some minor revisions as specified below. These minor revisions include some improvements to the mechanistic understanding and providing more information on how to interpret these laboratory results within the

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context of how SOA forms from isoprene + NO<sub>3</sub> in the ambient atmosphere.

#### Specific Comments:

Page 5, 149. From the measurements of RO<sub>2</sub>, HO<sub>2</sub>, and NO<sub>3</sub>, can you approximate the fate of the RO<sub>2</sub> radical in your experiment? Were conditions such that the RO<sub>2</sub> predominantly reacted with another RO<sub>2</sub>, NO<sub>3</sub>, or HO<sub>2</sub>? Do you have an estimate of the lifetime of the RO<sub>2</sub> radical in your experiments and how this compares to the RO<sub>2</sub> lifetime in the ambient atmosphere. RO<sub>2</sub> radical lifetime is often longer in the atmosphere compared to experiments. Would this possibly enhance the SOA yield for ambient conditions for HOMs?

Page 5, line 160. Please provide more detail here on using the H<sub>2</sub>SO<sub>4</sub> sensitivity for the HOMs. Are there certain HOMs this assumption would apply more too? For example, does this assumption apply more to HOMs that are more oxygenated or have a higher C\*? Please specify the overall uncertainty in HOMs in the main text (It looks like you calculate this in the supplement). Is there need to add uncertainty here for using the H<sub>2</sub>SO<sub>4</sub> sensitivity directly for the HOM sensitivity?

Figure1. Please add the names for the top m/z on panel b like done for panel a. It looks like many of the top m/z's are the same, but maybe some are unique. It's hard to compare by eye because the m/z lines are so small. Coloring the m/z label by their type listed in the pie chart would also be useful for the reader.

Page 11 line 292: Because you can measure OH and NO<sub>3</sub>, can you approximate how much isoprene and the first-generation NO<sub>3</sub> nitrates react with OH versus NO<sub>3</sub> in your experiments? This may lend insight into the products you are detecting. For example, the C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> compounds mentioned above seems more likely to form from OH oxidation than the H-shift in scheme S1a and S1b (Kwan 2012 Fig 5)? The reaction rate constant for the first-generation nitrates reaction with NO<sub>3</sub> is low compared to OH rate constant (Wennberg 2018). From this information, can you connect how your laboratory results should be interpreted to the ambient atmosphere? For example, how long lived are

NO<sub>3</sub> derived first-generation nitrates in the ambient atmosphere are they likely to react again with NO<sub>3</sub> or with OH at dawn?

Adding pictures of the molecules to schemes S1-S4 would be very beneficial for the reader.

Page 13 line 350. Can you explain how this statement connects with these schemes more. I do not follow as both scheme 2 and scheme 3 have an example of a nitroxyhydroperoxide and a hydroxy nitrate? Also the likelihood of each pathway being relevant in your experiments seems more related to the RO<sub>2</sub> fate (i.e., reaction with another RO<sub>2</sub> or HO<sub>2</sub>) than with the loss rate of nitrooxy hydroperoxides and hydroxy nitrates in Ng et al., 2008. Can you include this into your explanation too?

Page 13 line 370: Is it also possible that instead of C<sub>5</sub> nitrooxy carbonyls reacting more slowly with NO<sub>3</sub> than C<sub>5</sub> hydroxy nitrates that instead less HOMs are formed from C<sub>5</sub> nitrooxy carbonyls because of the carbonyl group leading to more fragmentation (e.g., in MACR OH oxidation H-shifts lead to losing CO - Crounse 2012)? Have you considered this?

Page 16 line 447: The rate constants for RO<sub>2</sub> + RO<sub>2</sub> reaction are heavily structure dependent, so this assumption does not really hold in atmospheric chemistry. This should be considered here. For example, in schemes 2 and 3, the dominant RO<sub>2</sub> isomers of C<sub>5</sub>H<sub>9</sub>N<sub>2</sub>O<sub>9</sub> and C<sub>5</sub>H<sub>9</sub>N<sub>2</sub>O<sub>10</sub> will not be the one pictured. The one pictured will most likely lead to HOMs. The dominant one will be the peroxy radical in the tertiary position, which will likely lead to fragmentation and not HOMs. This tertiary peroxy radical will react with other RO<sub>2</sub> much more slowly than secondary or primary peroxy radicals (Jenkin 1998, <https://doi.org/10.1023/A:1005940332441>), so you would not necessarily expect very much ROOR from these RO<sub>2</sub> radicals even though they are dominantly detected. Have you considered this?

Page 21 line 588: How was this HOM yield calculated? Is it from the first injection of isoprene or over the entire experiment?

Conclusions: As related to the questions above, please include in more detail how to interpret these laboratory results within the context of how SOA forms from isoprene + NO<sub>3</sub> in the ambient atmosphere. How do your laboratory conditions compare to the ambient atmosphere (e.g., RO<sub>2</sub> fate (reaction with NO<sub>3</sub>, RO<sub>2</sub>, HO<sub>2</sub>, isomerize), RO<sub>2</sub> lifetime, fate of the first-generation organic nitrates reaction with NO<sub>3</sub> at night or OH at sunrise)?

Technical comments:

Scheme 2a: missing NO<sub>3</sub> group on second molecule. In Scheme 2b, is the 3rd label really a H-shift? It looks like this should be reaction with RO<sub>2</sub>/NO<sub>3</sub>?

Scheme 3b: missing NO<sub>3</sub> group on second molecule. And the last molecule OOH should be OH?

Page 9 line 235 there are two “in”

Figure S3, isoprene is spelled incorrectly.

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