

We thank the reviewers for their comments and suggestions on the manuscript. We outline below responses to the points raised by each referee and summarize the changes made to the revised manuscript. We also provide a revised version of the manuscript with highlighted modifications.

## Responses to RC1

*The authors present a well-conceived and thorough chemical mechanism for gas-phase oxidation of naphthalene and for the resulting SOA formation. Comparisons are made between the mechanism and results from an OFR reactor. This is a very thorough and careful study, with much attention to detail and to what is available in the literature. The work is well presented, with (among other things) a very logical structure and naming system. I recommend publication, subject to consideration of the comments below.*

*My first comment is really the only one of significance: It is true that GECKO-A does not handle naphthalene or PAH's in general. That said, once the aromaticity of one of the fused rings is broken (e.g., from OH addition), the GECKO-A website appears to me capable of at least dealing with the remainder of the species encountered here, albeit without full recognition of all the aromatic-like chemistry that ensues in some cases. At a quick glance, it did look to me though that species like 2NaOort and 2NaOpar were treated in GECKO-A as is done in this work. Also, MechGen (<http://mechgen.cert.ucr.edu>), conceptually similar to GECKO-A, appears to treat naphthalene chemistry explicitly (although I know much less about the details). So, while I am sure that there are still many unique aspects to the current work, I think that at the least some mention of the other systems and comparisons with them should be done. (I realize that a brief mention of this is made near the end of the paper, dealing with continuation of the chemistry beyond what is outlined in this manuscript).*

The mechanisms of MCM, GECKO-A and Mechgen are mostly based on the same SARs, in particular those of Jenkin et al. (2018a, b and 2019) for estimating the reactivity of compounds with OH or the reactivity of RO<sub>2</sub>. For aromatic compounds, these SARs have been developed on the basis of available experimental data, which do not include PAHs. While these SARs are technically applicable to carbons common to several aromatic rings specific to PAHs, it has not been established that this makes sense chemically and that the reactivity of these compounds can be represented with these SARs without introducing significant uncertainties. This is one of the reasons why MCM and GECKO-A, developed by the same teams as these SARs, do not represent the reactivity of PAHs. MechGen technically represent the first oxidation step of naphthalene by OH by directly applying the SARs (with the interrogations and limitations mentioned above). However, it is mentioned in the MechGen documentation (Feb. 2024) that the compound “with unknown mechanisms like [...] naphthalenes” “are not currently handled by MechGen”.

About the comparison with GECKO-A, as mentioned, the present development only takes into account the first oxidation steps, which are not included in GECKO-A, which can then be used for the chemistry of secondary compounds with 1 aromatic ring or less. About the 2NaOort and 2NaOpar compounds you mentioned, except for the proposed new pathways, the Jenkin et al. (2019) RO<sub>2</sub> SAR as implemented in GECKO-A was used to estimate the kinetics of “classical” RO<sub>2</sub>/RO pathways (also note that GECKO-A have difficulties to generate the entire mechanism of 2NaOort) so GECKO-A and the present mechanism have a lot in common.

*Remaining comments and suggestions:*

*Line 12: Perhaps change text to read: “Its atmospheric oxidation products are oxygenated compounds potentially harmful for health and/or for contributing to secondary organic aerosol ...”*

The verb was missing, text was modified.

*Line 103: “A rate coefficient of ...” would sound better.*

*Line 106: ‘includes’ is spelled incorrectly.*

Text was modified.

*Line 128: I think the term ‘carbonyl radical’ is used on some occasions when what is really meant is ‘carbon-centered’ radical.*

You are right, correction was made in the entire text.

*Figure 3 (for example): The ring-closure chemistry is being applied to radicals of structure R-COCO(.). Could CO elimination occur with these species, as happens with CH<sub>3</sub>COCO(.) formed from methylglyoxal?*

We clearly forgot to take this into account in our mechanism. This is corrected in the figures, text, results and supplements. However, this only has little impact on the compounds formed or the mass of SOA (now 6.0 instead of 5.8  $\mu\text{g m}^{-3}$ ), as it mainly affects the chemistry of three species PhDKKD (less than ~1% of the total oxidized matter), PhDKKD (less than ~0.7%) and a fraction of PhODKD (less than ~2%).

*Since NaOPEN is a major product, it must be formed somehow, but the H-shift shown in Figure 4 (middle left) doesn’t seem quite right to me. (The first step, moving H from the alcohol to the hydroperoxide is very likely endothermic).*

The pathway was proposed by Kautzman et al. (2010) to explain the high amount of NaOPEN experimentally observed. The rate coefficient is here  $1.0 \times 10^{11} \times \exp(-9750/T)$  and is estimated following the Jenkin et al. (2019) SAR. In his article Jenkin mentioned that the rate is “Based on rate coefficients reported by Peeters et al. (2014) for corresponding unsaturated secondary and tertiary -hydroxy peroxy radicals formed in isoprene oxidation. Applied generally to unsaturated -hydroxy peroxy radicals containing the substructures shown.”

*Line 255: should be 18%, not 12% I think.*

It is a typing mistake, text was modified.

*Line 257: I think you mean by HO<sub>2</sub> elimination, not hydrogen abstraction?*

You are right, text was modified.

*Overall, the figures are very clear and well labeled. There are a few places however where additional labeling can be done – e.g., 2NaOOBp in Figure 7. Also, the different cases could be labeled in Figure 8 to further guide the reader.*

Missing labels were added, and a general labeling is added in fig 8.

*It appears to me that the ring closures proposed are in most cases competing with very fast processes, such as O<sub>2</sub> addition to an RCO radical or CO<sub>2</sub> elimination from RCO<sub>2</sub>. Can the authors provide any further justification for these processes? (I would guess that the competing processes are happening on sub-microsecond time scales).*

It is very difficult to measure and therefore compare the rates of such reactions. However, due to their radical and intramolecular nature, it is reasonable to assume that they are indeed fast. Consideration of the ring-closing reaction pathway stems first and foremost from experimental observations showing the

significant formation of phthaleic anhydride (PhAnhy) during naphthalene oxidation. These observations led Kautzman et al. (2010) to propose, in a simplified manner and without kinetics estimations, the ring-closure pathway for phthaleic anhydride. Similarly, Bloss et al. (2005) observed a high concentration of maleic anhydride during photolysis of butenedial during benzene oxidation (photolysis causing the H-removal from one of the aldehyde groups). These observations seem to confirm the competitiveness of the two pathways. We chose then to apply the same logic as Bloss et al (2005) and, due to the lack of data on naphthalene, we applied the same branching ratios as them for competition with O<sub>2</sub> addition and CO<sub>2</sub> elimination, not only for PhAnhy formation but also whenever a similar situation arose. As mentioned in the “limits and perspectives” section, it will be important in the long term to review and adjust these ratios when more experimental data become available for comparison.

*Line 325 – I think you mean acyl peroxy here, rather than acyloxy.*

Text was modified.

### References:

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## Responses to RC2

*This manuscript is well-written, providing clear and thoroughly documented step-by-step explanations of the detailed gas-phase chemical mechanism for naphthalene in the atmosphere. The reaction schematic figures are clear and organized, and the naming system for radicals and products is straightforward and easy to follow. Beyond the mechanism discussion, the authors also show a reasonable agreement between predicted products and observed data in earlier studies. Even though, I found the mechanism evaluation part is insufficient, I still recommend publication after addressing the following comments:*

*1. As I mentioned, I am concerned about the insufficiency of the mechanism evaluation. I totally understand the limited studies on naphthalene and its major products. But I would still recommend a more comprehensive evaluation if data is available.*

There is no other precise speciation and partitioning data in the literature concerning the compounds studied here. Experiments similar to those presented and analysed for toluene in the article by Lannuque et al. (2023) are planned in the coming years. The data from future experiments can be compared with new simulations using the mechanism, allowing it to be evaluated and improved.

*2. From my understanding, explicit mechanism generation tools should have the capability to handle carbonyls. Have the authors examined these tools to compare their proposed mechanisms for PhODKD and PhDKOD? If not, it might be valuable to conduct such an examination and compare the mechanisms. If already done, I would be interested to learn if there are any discrepancies between the proposed mechanism here and those predicted by MCM, GECKO or MechGen.*

The development of our mechanism for the radical and aliphatic chemistry parts is largely based on the work and SARs of Jenkin et al. (2018a and 2019) as is the MCM, GECKO-A or MechGen and the first two were used extensively during development. MCM does not represent the chemistry of PhODKD and PhDKOD and GECKO-A was used to estimate reaction pathways and rates. The main difference in the treatment of these compounds with GECKO-A is here the introduction of the ring closure pathway. However, the estimation of the radical intermediate steps of this new pathway was done using the SARs of Jenkin et al. (2019) as implemented in GECKO-A.

*3. The authors had a statement that “there are no precise mechanistic or kinetic data for hydroxynaphthalene (NaO) oxidation”. However, based on a quick search, I don't believe this statement holds true. Please check this work: <https://doi.org/10.1021/es960813g>. Given the uncertainty surrounding this statement, I would recommend that the authors re-examine their NaO mechanism by doing a more careful literature review.*

You are right, Bunce et al. (1997) article you mentioned is already cited in the article for the general work on naphthalene. Bunce et al. (1997) work is mainly centered on the first oxidation step of naphthalene than naphthol. They only mentioned and proposed one way of oxidation for the naphthol by OH: the attack of the alcohol group without giving more details on competitive pathway (and so branching ratio). The method we have used enables us to establish branching ratios between the various possible oxidation pathways, while obtaining an overall coefficient rate of the same order of magnitude as those of Bunce et al. (1997). The sentence is too categorical and has been modified: “*Bunce et al. (1997) experimentally estimated a  $k_{\text{NaO}+\text{OH}} \approx 5 \times 10^{-10} \text{ s}^{-1} \text{ molec}^{-1} \text{ cm}^3$  but, to the best of our knowledge, there are no study providing detailed and combine mechanistic or and kinetic data for NaO oxidation.*”.

More generally, on the one hand there are numerous articles proposing oxidation pathways to explain experimental observations of particular compounds without considering possible competitive pathways or giving rate coefficients, and on the other hand articles giving measurements or estimates of rate coefficients without proposing a precise mechanism, yet both are necessary for accurate modeling work.

*Other minor comments:*

*Line 50: Is this limitation because these mechanism generation tools typically only process aromatic adducts with a single ring? Did you check MechGen?*

The mechanisms of MCM, GECKO-A and Mechgen are based on the same SARs, in particular those of Jenkin et al. (2018a, b and 2019) for estimating the reactivity of compounds with OH or the reactivity of RO<sub>2</sub>. For aromatic compounds, these SARs have been developed on the basis of available experimental data, which do not include PAHs. While these SARs are technically applicable to carbons common to several aromatic rings specific to PAHs, as MechGen can do, it has not been established that this makes sense chemically and that the reactivity of these compounds can be represented with these SARs without introducing significant uncertainties. This is one of the reasons why MCM and GECKO-A, developed by the same teams as these SARs, do not represent the reactivity of PAHs.

Similarly, theoretical studies of reactivity are possible, as mentioned in the article (Zhang et al. (2012) for example). However, these theoretical models have also been developed on data from mono-aromatic compounds, and the application of such models to PAHs is questionable and the uncertainties difficult to quantify. This brings us back to the problem raised in question 1: there is a lack of precise, quantified data on PAH oxidation, both for the development of theoretical reactivity models and for SAR or chemical mechanisms. This is largely what imposes the limitation raised here.

*Line 125: The Shiroudi et al. (2014) paper suggested 92% at position 1, but I believe using 90% here is totally acceptable.*

Shiroudi et al. (2014) used two theoretical methods to estimate this branching ratio at 1 bar and 300K: TST method giving a 89.6 / 10.4 ratio and RRKM method giving a 92 / 8 ratio. Because of these uncertainties, we have chosen the simpler, rounded value for the ratio (90/10). The ratio for naphthol in Figure 1 is an error and has therefore been corrected (this has no impact on the rest of the mechanism, as only one isomer is considered for simplification).

*Line 140: Even though I finally got through this, I still find both the context and Figure 1 a little bit confusing, especially by combining the two isomers when calculating the yields.*

We understand the confusion, the choice to regroup the isomer was made to limit the number of molecules and reactions in the already complex mechanism. The branching ration integrate both the yield from OH attack on the different carbon and the different possible reaction with O<sub>2</sub> after that. Normally carbon centered radicals as 4NaO are not represented in mechanism considering the rapid reaction with O<sub>2</sub> but here we choose to keep this step to represent the possible reaction with NO<sub>2</sub> instead of O<sub>2</sub> which is the only way to form the nitronaphthalene.

*Line 375: In Figure 10, it took a while to realise that the labeling of the oxygen atoms and molecular weight (MW) is shared between the two figures but plotted separately. Is there a better way to present the legends?*

This figure construction was chosen to be consistent with the one of a previous paper published in ACP about toluene oxidation experiments and modelling. (Lannuque et al. 2023). We thought about putting the legend for the labelling of oxygen atoms below the left column, and the legend for the labelling of molecular weight below the right column, but it uses significant extra-space and does not improve readability.

## **References:**

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