We want to acknowledge the reviewer's time and effort to review the submitted manuscript. In the following we will address the review comments in a comment by comment – fashion: review comments are represented in bold letters (e.g., "**This manuscript…**"), replies by the authors are marked by an "Author's response:" and changes made to the text are written in color (e.g., "Computer simulations of a flow tube…"). To ease following the changes made in the manuscript, they are highlighted in the updated files. References used in the answers to reviewers' remarks are listed at the end of this file.

The main part of the manuscript is referenced with a "MS" and the supporting information is referenced with "SI". All line numbers referenced by the authors refer to the updated manuscript files.

Review 1:

(received 24th of August, 2023)

"A method is presented for including autoxidation chemistry in detailed explicit chemical mechanisms. Using the oxidation of benzene, as represented in the Master Chemical Mechanism (MCM), as a starting point, autoxidation chemistry involving H atom shift isomerization reactions and association reactions for peroxy radicals is included, along with competing reactions. The mechanism is guided and constrained using distributions of product species masses obtained in laboratory studies, using CIMS, with the OH-initiated oxidation of benzene used as a "proof-of-concept" example. Vapor pressures are estimated for the closed-shell product species, to allow gas-particle partitioning to be represented, and the resultant simulations of SOA formation provide a good description of the laboratory results. The mechanism is also applied in a trajectory model to simulate the chemistry development and SOA formation on trajectories arriving in southern Sweden in April 2021, with the results confirming an important contribution from benzene-derived species formed from the autoxidation chemistry.

This paper considers an important topic, and provides an interesting discussion and illustration of the complexity of autoxidation chemistry and its role in SOA formation. However, I do have some concerns about the details of the generated mechanism and the identities of the species it contains, and the practicalities of applying the methods more widely to the range of precursor VOCs that contribute to SOA formation. These are outlined in the following comments."

Author's response: The authors find their work well represented by the summary above and look forward addressing the issues raised by the reviewer.

"1) Is the aim to create a genuine "mechanistic understanding" of autoxidation or a practical tool? At present the method seems to fall somewhere in between and do neither properly. Outside its ability to describe a particular experiment it is optimized and constrained to, it does not really move mechanistic understanding forward in that some of the core reactions seem to be mechanistically impossible, and the (optimized) parameters assigned to the

isomerization reactions cannot therefore be rationalized in terms of what is predicted for actual species (e.g., by methods such as Vereecken and Noziere, 2020), or compared to those predictions."

Author's response: The aim of the proposed method (autoAPRAM-fw) is to serve as a tool enabling the creation of lumped chemical reaction schemes. It is based on theoretic knowledge of chemical reaction types considered relevant for the system, as well as on NO_3^- CIMS data. An important aspect of the framework is the degree of automatization, allowing it to handle large numbers of chemical reactions. Practically, the method can assign the observed evolution of a chemical peak list to (theoretically) suggested reaction types.

In the present approach for benzene, there is a single path for autoxidation for all peroxy radicals of similar molecular composition (i.e., there are no RO_2 - isomers). We are aware of the consequences: the choice of structure for the representing molecule does not describe the variety of species present (see e.g., MS, l. 117f. "autoSMILES may be rerun to investigate the effect of varying structures of input-RO2 isomers."). Note that the autoAPRAM-fw is not limited to a single isomeric representation of RO2 species. A generally unlimited number of RO2 isomers may be considered.

We do agree that the RO2 species (of similar atomic composition) described in the present benzene scheme do miss a structural diversification, as they are represented by a single structure. However, reaction rate coefficients valid for the group of species may still be compared to structure-activity relationships (SAR) targeting the reaction rate coefficient for a single structure and reaction type: it is done to support the plausibility of the "potential solutions" (see MS, l. 151 f.) derived with this method. It is not the author's intention to prove the rate coefficients correct.

"Consider the initial set of autoxidation initiation reactions:

{1} BZBIPERO2 -> BZo_RO2_O7

{2} BZBIPERO -> BZeo_RO2_O6

{3} BZBIPERO2 -> C5_RO2_O6 + CO

{4} BZEMUCO2 -> BZeo_RO2_O8

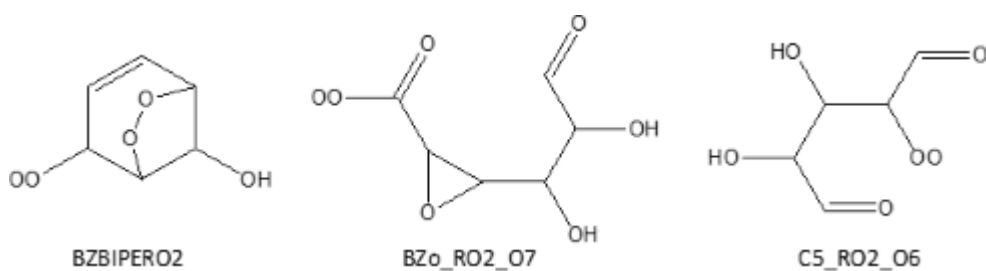
{5} BZEMUCO2 -> C5_RO2_O7 + CO

{6} PHENO2 -> BZeo_RO2_O8

{7} PHENO2 -> C5_RO2_O7 + CO

The species BZBIPERO2 is the main peroxy radical formed from OH + benzene, which has been observed (e.g., Elrod, 2011). However, the products of reactions {1} and {3} cannot be formed from it (and they do not contain the expected -OOH group).

BZBIPERO2   BZo_RO2_O7   C5_RO2_O6

"

Author's response: We do agree that some of the molecule structures in the suggested autoxidation chemistry scheme may not form from their (formal) precursors. This on the one hand is a result of the representation of the peroxy radicals (in the present benzene chemistry, we do not consider RO2 isomers => all RO2 species with the same atomic composition are assigned a single structure). On the other hand, the isomeric distribution of benzene peroxy radicals, although being an intensively studied system, is not fully understood yet. As a result, we based the initiation of the autoxidation chemistry on radicals that form in MCM.

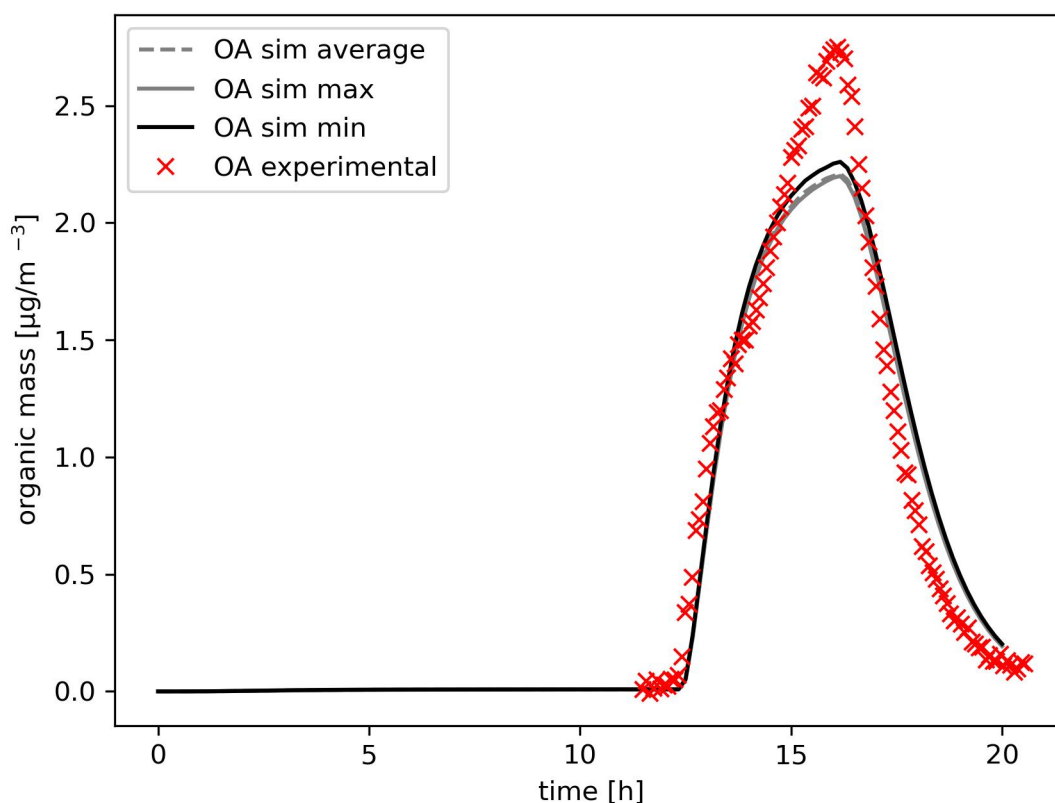
We do not agree with the reviewer's claim that the products shown in the above figure may not form from the BZBIPERO2. We do agree, it is questionable whether these structures can form in an unimolecular (ignoring the addition of O_2) reaction at the rates assigned.

Regarding the claim for the presence of an -OOH group: we do agree with the reviewer that a peroxy radical with 7 oxygen atoms, forming from a rearrangement of the BZBIPERO2 is expected to contain an -OOH functional group. Again, the species structure chosen in this work is a single representative of the isomeric distribution of all O7-RO2 species. It was randomly selected from the variety of peroxy radicals we considered (see Fig S12 in the SI).

"As a result, the subsequent sequences of reactions, following isomerization of this main peroxy radical, generate an incorrect set of closed-shell product species, for which the vapor pressures are then rigorously estimated to allow SOA simulations. This cannot be regarded as predictive. In passing, it is noted that peroxy radical isomerizations can also proceed by ring-closure (addition to a double bond), and might this more likely be the case for species like BZBIPERO2?"

Author's response:

We thank the author for raising this point: We do agree that some of the closed shell species may well have wrong structures. However, the present approach is based on the hypothesis that the description of autoxidation is much more relevant to the formation of SOA than the exact description of chemical structures. We added the plot below to the SI ("Fig S18 depicts variation of organic aerosol "OA" simulated (seeded JPAC low-NOx experiment) based on three different sets of underlying RO_2 structures. For each atomic composition, the isomers with lowest ("OA sim min") and highest ("OA sim max") satuartion vapor pressure are considered. An average value of isomeric Psat distribution forms the basis for simulation "OA sim average". The underlying set of structures (including closed shell structures and adducts) are based on RO2 structures described in

Fig. S12.") supporting this hypothesis. For the JPAC low-NOx experiments, there is hardly any difference in SOA formation. This variation in SOA formation arises from the maximum difference in p_{sat} based on all potential structures described in SI Fig/scheme S12. Accordingly, for the present situation, the structural differences do not strongly impact the SOA formed. The choice of p_{sat} representation method seems more relevant (see MS Fig 3 a,c,e) . Most relevant, in the present system is to consider autoxidation reactions at all (see MS Fig 3 b,d,f). We added the following statement to the Discussion and Conclusion section: "Clearly, the molecular structures and their isomeric distribution are subject to speculation. Likely, this situation will remain for unforeseen time. Similar, the exact retrieval of saturation vapor pressures for given molecule structures is difficult. However, based on the set of potential peroxy radical isomers (see Fig. S12) and the methods applied to derive the saturation vapor pressure (see section "2.5 Deriving the saturation vapor pressure"), we found that the description of autoxidation and its effect on the molecular structures is still crucial for modelling SOA formation from benzene. This is valid, independent of the choice of underlying RO_2 structures and independent of the choice of p_{sat}-derivation method."

We do agree that ring-closure (e.g., as described in Motta et al. (2002) or as suggested by Molteni et al., (2018) for aromatics), might be a possible isomerization reaction, though the energy barrier for formation is very high: about 40 kcal/mol according to Motta et al., (2002) or Xu et al. (2020). However, note that we do not claim either to cover all potential pathways, nor to pick the most relevant species structure. The suggested method is based on structures picked from a pool of RO2 species potentially forming in the benzene autoxidation chemistry (see SI, Figure S12/scheme for the RO2 structures-pool considered in the present work). The closed shell species (including

adducts) structures are derived from these peroxy radicals considering reaction types R1 to R9 (see MS, 2.2 Setting up the gas-phase chemistry).

"Some of the same is also true for the other starting peroxy radicals, BZEMUCO2 and PHENO2, which each isomerize to the same pair of peroxy radicals (BZeo_RO2_O8 and C5_RO2_O7), despite these not being products that cannot obviously be formed from either BZEMUCO2 or PHENO2 (although these do contain -OOH groups)."

Author's response: See previous answers where we discuss the role of single RO2 representatives and the meaning of their atomic structures.

"There is a limited series of subsequent isomerization reactions forming progressively more oxidized peroxy radicals. However, most peroxy radicals in the mechanism react by the set of conventional reactions (e.g., with NO, HO2, RO2), with RO2+R'O2 association reactions also added. However, it is not clear what criteria are applied to decide which isomerize and which do not. As indicated above, it does not seem to be related to peroxy radical structure and the isomerization reactions that are predicted/expected to be available."

Author's response: The same set of reactions are typically applied to all RO2 species generated with autoAPRAM-fw. As each RO2 species (of the RO2 generated by the autoAPRAM-fw) represents a variety of RO2 isomers, no reaction pathway can be excluded based on structural considerations (unless these are valid for all potential structures of that atomic composition). Details on the gas-phase chemical reaction types are given in the MS, section "2.2 Setting up the gas-phase chemistry".

"Regarding its practicality as a tool, inclusion of autoxidation chemistry inevitably increases the complexity of the mechanism substantially. In MCM, complete benzene degradation (i.e., notionally to CO2 and H2O) is treated by 406 reactions of 149 species, which is regarded as far too complex for most practical atmospheric models. The ADPRAM module adds 934 reactions and over 800 species. In practice, some of these species are closed shell products that are sufficiently volatile to react (e.g., with OH) in the gas phase, and these reactions are ideally required for a complete description – so it is not even a full description. The point here is that the added autoxidation chemistry inevitably causes an explosion of complexity, so that the mechanism is even more remote from being able to be used in most practical atmospheric models – and it only considers one of many precursor VOCs."

Author's response: We agree that the current version of the benzene autoxidation chemistry strongly increases the number of reactions describing the benzene chemical system. However, since the current MCM representation is not producing the species observed (in SOA), some addition is needed. We do agree as well on the judgement of the reviewer designating the scheme as "...not

(even) a full description". A full description is targeted by other approaches (e.g., The Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A)[1]).

The increase in complexity is expected. As stated in the "Discussion & Conclusions" section (MS, l. 581 f.), we aim to formally reduce the code once it is capable to reproduce the experimental findings properly. This approach is described in an article by Kaduwela et al. (2015). However, this is beyond the scope of the present work.

"2) The trajectory model simulations highlight an important contribution resulting from the NO3-initiated oxidation of the nitro-catechol product in MCM, specifically resulting from association reactions of the product peroxy radical, NNCATECO2. Although this is an interesting observation, it should be noted it is not clear if this species is actually formed from the NO3 + nitro-catechol reaction. The preceding MCM chemistry systematically oxidizes phenol to aromatic products containing increasing numbers of polar substituents, with an arbitrary limit of three substituents (-OH or -NO2). For practical reasons, the subsequent chemistry then aims to produce ring-opened species that promote break down to smaller species. NNCATECO2 is therefore produced as the first step in this break down process, assuming the chemistry proceeds analogously to the main OH + benzene oxidation sequence. Some caveats should probably therefore be included for this result."

Author's response: We do agree that the SOA formation initialized by NO3 oxidation of substituted MCM species is lacking experimental evidence. We mention this in the Discussion and Conclusion section (line 568: "This effect has not yet been investigated experimentally."). However, to stress this issue and to avoid misinterpretation, we added some more caveats to the model results on the this SOA formation path:

"Additionally, a prompt increase, driven by the NO_3 radical, is predicted by the model at dawn. This increase has not yet been explored experimentally and questions the applicability of the widely accepted concept of OH-based SOA mass yield in the atmosphere." MS, lines 31 ff

"There is a distinct increase in modeled SOA mass after sunset" MS, lines 460 f.

"Note that this formation pathway remains to be investigated experimentally. Yet, it is entirely based on modeling results." MS, line 468

"Note that the benzene-SOA formation initialized by nitrate radicals, yet, is a model prediction and remains to be examined experimentally." MS, line 558 f.

"Other comments

Line 47: For clarity, "particular" could be replaced by "particulate" – in particular because "particular", in its more general meaning, is used in the preceding sentence (and at other points in the manuscript)."

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[1]   https://geckoa.lisa.u-pec.fr/index.php (visited Nov. 2nd, 2023)

Author's response: We agree and changed "particular" to "particulate". MS, line 47

"Line 183: Many (probably most) acyl radicals add O2 to form the corresponding acyl peroxy radical rather than decomposing by loss of CO."

Author's response: In the manuscript, we do not make a general, quantifying statement on branching of the acyl radical towards a) the acyl peroxy radical and b) the pathway to CO scission. We do agree, possibly, this pathway is minor for many or even most acyl radicals. However, several works have suggested this pathway (e.g., Crounse et al., (2012), Jagiella et al.,(2000)) which provides a potential explanation for the formation of C5-species. This is why we include it in this work and assign rate coefficients that explain the observations.

"Line 198: The primary beta-hydroxy and primary alkyl plots in Fig. S10 do not seem to tally with those presented in Fig. 3 of Jenkin et al. (2019). The former seems to be elevated by an order of magnitude. The latter seems to be presenting that for secondary alkyl. "

Author's response: We thank the reviewer for pointing out this error in the reproduction of k-rates from Jenkin et al. (2019) article. We updated Figure S10 in the SI.

"Supplement, page 4: The information on the benzene scheme states that the rate coefficient units are "cm3 molecules-1 s-1 if not stated differently". As far as I can see, there are no examples of "stated differently" even though many of the early reactions should presumably have units s-1."

Author's response: We thank the reviewer for highlighting this discrepancy. We agree, the unit-description is not consistent with rate coefficients for unimolecular reactions.

We added unit descriptions to the following reactions: {1} to {7}. Further we added unit descriptions to the following reaction categories: R1, R2, R6 - R9 :

"Reaction rate coefficients are given in s^{-1} for reactions {1} to {7} and reaction types R1, R2 and R6 to R9 (see main manuscript section 2.2 for more information on the reaction types considered). All other rate coefficients are given in $cm^3 molecules^{-1}s^{-1}$. "

"References

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Jenkin, M. E., Valorso, R., Aumont, B., and Rickard, A. R.: Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction, Atmos. Chem. Phys., 19, 7691–7717, https://doi.org/10.5194/acp-19-7691-2019, 2019.

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Review 2:

"This manuscript described a framework to model gas-phase autoxidation chemistry and to predict the secondary organic aerosol (SOA) formation. This framework was tested on benzene oxidation under both laboratory conditions and ambient conditions. This study addressed an important topic, autoxidation, and aimed to link gas phase chemistry to aerosol formation. However, the major finding in the manuscript, which is that autoxidation explains nearly all benzene SOA under low-NOx conditions, contradicts previous experimental findings in the literature. This issue must be addressed before I can recommend it for publication."

Author's response: We thank the reviewer for their critical remarks and we're eager to address the raised issues carefully!

"Major Comments.

1. **Previous chamber experiments have demonstrated that phenolic pathway contributes to aromatic SOA formation[1-3]. The experimental benzene SOA yield is about 20% under high NOx conditions where RO2 autoxidation is suppressed[2], which is a manifestation of the phenolic contribution of SOA. And previous studies have estimated that phenolic pathway contributes to 20-40% of benzene SOA under low-NOx conditions. Thus, the discrepancy between this study and previous findings needs to be addressed/discussed. It is highly possible that the SOA yield from the phenolic pathway is underestimated in the model, given the modeled SOA yield under higher NOx condition is only 1% (Line 466), much smaller than the 20% yield in the literature. In addition to adjusting the reaction rate coefficients based on NO3- CIMS measurements, the measurements of phenol, catechol, etc. also provide critical constraints on model performance.**"

Author's response: We fully agree: The question how the present work relates to prior findings is considered very important by the authors as well.
Ng et al. (2007) report a benzene SOA yield of 28.1 +/- 0.9 % under high NOx conditions. We refer to their work in sections "2.6.4 Parametric yield study", "3.2 Partition to the particle phase", "4 Discussion & Conclusions", as well as in the SI section "High NOx conditions". Further, we discuss potential reasons for the discrepancy between SOA yield observed and simulated.

The work by Nakao and co-authors reports "that approximately 20 % of the SOA of benzene, toluene, and m-xylene could be ascribed to the phenolic route under low NOx conditions" (Nakao et al., 2011). In section "3.2 Contribution of phenolic route" they estimate the potential contribution of phenolic products to benzene SOA formation. This estimate is based on a) the expected benzene and phenolic species turnover; and on b) the experimentally determined SOA yields for benzene and phenol upon OH reaction. Accordingly, the "phenolic route" yields 23.5% +/- 4.7% of SOA. Unfortunately, the present approach does not allow to separate the yield via phenolic route from other reaction pathways. As a result, we can't derive a number for the phenolic pathway in the experiments simulated.

Schwantes et al. (2017) describe the formation of SOA from toluene and cresol oxidation. Although an aromatic compound, toluene chemistry does not directly compare to benzene chemistry (see e.g. Iyer et al. 2023). Accordingly, we consider the work to be conceptually relevant to the present topic of benzene autoxidation. However, quantifications are not to be transferred.

The authors do agree that benzene SOA seems to be suppressed under high-NOx conditions and that RO2 autoxidation is suppressed. However, we do not share the conclusion that the difference between low NOx and high NOx SOA yield is explained by the "phenolic route". Similarly to the benzene (aut)oxidation chemistry, the phenol chemistry is affected by a strong RO_2 reduction through NO as well. As a result, the contribution via the "phenolic route", likely, will also change for changed NOx conditions. Further, we want to state that the "phenolic route" is considered in the present model. Clearly, it does not allow us to explain the SOA found under high NOx conditions. The authors don't see an indication that the phenolic pathway is the key process (See discussion on potential reasons for the discrepancy in SOA in section "4 Discussion & Conclusions" and SI-section "High NOx conditions").

We do agree that the SOA formed via the phenolic pathway may be under-represented. However, the mentioned difference between modelled and observed SOA formation under high NOx conditions is not considered a strong indicator. Further, the mentioned 1% SOA yield under extreme atmospheric-like conditions should not be compared to experimental findings under strongly differing conditions.

We do agree that the measurement of phenolic species may provide additional constraint to test model performance. However, a better quantification of radical formation via these pathways would only replace the current calculations covered by MCM. It would not add an entirely new pathway.

"

2. **The manuscript describes the adjustment/tuning of reaction rate coefficients in detail. Is such adjustment required for each VOC system? If so, the deployment of the proposed framework could be quite cumbersome. The adjustment is based on comparing the simulated mass spectra to measured mass spectra by NO3- CIMS in flow tube experiments. If the HOMs contribute significantly to SOA, several questions arise. First, how much SOA is produced from the flow tube experiments? Second, given the NO3- CIMS only measured the gas-phase HOMs, does the simulated mass spectra consider the gas/particle partition?** "

Author's response: Yes, the tuning of rate coefficients needs to be done for every VOC system, unless we have a full set of SARs to equip the equations with rate coefficients. We agree that the tuning of the rate coefficient represented a bottleneck in the present work. However, we currently

develop two independent methods to tackle this issue: 1) a randomized search for good fits of rate coefficients; and 2) an analytical solution to obtain rate coefficients from stationary and steady-state – like experimental conditions. While 1) requires significant computational effort, appraoch 2) can solve a comparable chemical system within seconds on a personal computer.

We added a statement to the conclusions section: "Currently, the fitting of reaction rate coefficients to allow for reproduction of the experimentally obtained gas phase species mass spectrum is a limiting factor: it requires a lot of manpower (of the order of weeks for a system like benzene). To overcome, we are currently exploring two approaches: 1) a randomized search for good fits of rate coefficients; and 2) an analytical solution to obtain rate coefficients from stationary and steady state – like experimental conditions. Approach 1) requires substantial computational effort while the analytical method can be run on a personal computer within seconds." MS, line 487 ff.

SOA does not seem to form in the flow tube experiments due to missing surfaces to condense on and due to the short time periods (the hydrocarbon typically passes the tube within a few seconds). Even in the JPAC low-NOx chamber experiment (mean residence time is about 45 min, i.e., 150 times longer residence time compared to flow tube), there is no relevant SOA formation before seed aerosol addition (see MS, Fig. 3A or Garmash et al., 2019).
In the chamber experiments, the formation of SOA as well as wall-partitioning of semi-volatile organics is considered. A detailed description of the representations is given in section "2.6.2 Chamber runs" in MS, lines 272 ff. and the references therein.

"
   3. **Please compare the tuned reaction rates to literature values or estimates from SAR. **"

Author's response: Before listing the parts where model reaction rate coefficients are compared to SAR or literature values, we want to stress the fact that molecular structures suggested in the manuscript typically represent a variety of isomers. Accordingly, structurally specific SAR may not be applicable.

How the assigned rate coefficients compare to reported values in literature is discussed in the sections "2.3 Reaction rate coefficients" and "4 Discussion & Conclusions" (both in the MS). It covers the reactions:

   • RO2 + NO → RONO2 and RO

   • RO2 + HO2 → ROOH and RO

   • RO2 H-shift

   • RO - H-shift

   • RO2 + RO2 → ROOR

"Minor Comments
   1. **Line 32-33. This sentence is confusing. If the modeled increase has not yet been observed experimentally, one would naturally imagine the model results may not be accurate. I assume what the authors tried to argue is that "the modeled increase in**

SOA formation from NO3 chemistry of benzene oxidation products has been not explored in laboratory experiments." "

Author's response: We agree that this sentence may be misleading and changed "observed" to "explored". MS, line 32

"

2. **Line 356. The model evaluation figures under elevated NOx conditions should also be included in the main text, not hidden in the SI.** "

Author's response: The reasons for not considering the JPAC high-NOx results in the main manuscript are: We consider this experiment less suited to derive rate coefficients as it is much more complex compared to the flow tube experiment. Particularly, the partition of RONO2 species to the chamber walls strongly depends on the choice of saturation vapor pressures. Further, we only fitted the RO2 + NO and RO → RO2 autoxidation reactions rate coefficients for this system.

As a result, we consider the results from this fit to be less accurate. This is the reason why the plot is found in the SI.

We added a statement on the elevated-NOx conditions fitts to section "3.1 Pure gas-phase simulations":

"Note that we consider the retrieval of potential rate coefficients from flow tube setup to be more accurate. The reason is the degree of complexity in mixing reactors featuring comparatively long residence times (processes to consider: chemical reactions, mixing, wall partitioning, nucleation, aerosol formation, in- and outflux). In comparison, the flow tube represents a "simple" setup (processes to consider: chemical reactions and limited wall interaction). Accordingly, we consider the derived rate coefficients to be less accurate. The only rate coefficients derived from the elevated-Nox experiments are reaction types R3 and R8 (see section "2.2 Setting up the gas-phase chemistry" for more information on the reaction types)." MS, lines 357 ff.

"

3. **Line 538. Yields up to 1000% or 100%? Also, please specify that this is "observed in models", not experimentally in the atmosphere.** "

Author's response: The yield is 1000%, we checked the computed value. We changed the sentence to: "As a result, apparent mass yields of up to 1000% are modeled for short periods in time." MS, line 556

Reference

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