We thank the anonymous Reviewer for the insightful comments and suggestions that provided us with the opportunity to improve our article. Our responses to the specific comments and changes made in the revised manuscript are provided below.

Reviewer 2 comments

The presented work examines the OH radical reactions of three terpenoic mono alcohols in the aqueous phase. The study is designed as a combination of experimental and model work and aims at the elucidation of reaction mechanisms and the kinetic evaluation of the investigated conversions. The experiments are very useful and help to estimate the influence of aqueous-phase chemistry in the formation of secondary organic aerosols. The addition of the kinetic evaluation allows the modelling of these pathways under realistic conditions to test the competition of aqueous channels to gas-phase conversion. As the formation of SOA is often regarded as pure condensation of gas-phase reaction products up to now, this work helps to evaluate multiphase chemistry. Although in general very useful, sections of this work should be revised before publication. The most important part would be section 3.1, which includes the discussion of the presented pathways. That part lacks detail and does not seem to be derived from a comprehensive discussion of theoretically possible pathways. If the authors can convincingly address the comments below, the manuscript might be suitable for publication.

Major comments

- Section 3.1 The experimental analysis are done by GCMS. Some of the products were identified by authentic standards, but it seems that for the vast majority, the observed ions and corresponding fragmentation pattern was used to derive closed shell products and consequently, derive the reaction pathway. It is not clear to me what the rationalization was for the specific reaction pathway. This should be described in much more detail.

- More to that point, the investigated compounds show some structural similarity with bridging carbon atoms in some and methyl groups. Yet, the presented reaction scheme is quite different for the different compounds. Especially H-atoms geminal to the hydroxyl group, secondary and tertiary carbons behave very differently. The authors showed results from the structure-activity-relationship calculation, but interestingly did not follow the results from that discussion in the pathways. It is very crucial for the presented pathways to explain why the pathways are not more similar and what the choice of products in the presented scheme is based on. It seems that OH does not attack at tertiary carbon atoms. Do the authors have any explanation or hypothesis?

- I would suggest to start the results part with a general section and then move to a description of the analytical results before introducing the derived pathways.

Author's response: We agree that the proposed mechanisms were not discussed in sufficient detail. Because these comments refer to the results and discussion section connected with the mechanism, a combined response and list of revisions in this section are provided.

The rationale for selecting specific reaction pathways was based on the intramolecular selectivity of OH, predicted with SARs for the precursors and all major products, as well as with mechanistic considerations. In aqueous solutions [1], the rates of H-atom abstraction by OH from primary, secondary, and tertiary C–H sites tend to be very similar [1], opposite to the same reactions in the gas phase [2].

The low and even non-existent selectivity of OH toward CH_x groups of different order in aqueous reactions was reported by Rudakov in 1981 and 1986 [3, 4]. More recently, this phenomenon was discussed by Monod and Doussin (2008), who stated that "all the k(CH_x) values fall in the same range" [1].

Therefore, in water, the reactivity of OH toward CH_x groups is governed not by the carbon order but by the local molecular environment. Strong hydration of OH, which greatly increases its effective size, together with solvent-cage dynamics, likely contributes to the lack of interplay between carbon order and intramolecular selectivity of OH in H-atom abstraction reactions [1, 4].

Furthermore, although partial $k_{OH_{aq}}$ values estimated with SAR for the H-atom abstraction from primary, secondary and tertiary CH_x groups were relatively similar, OH attack on alkyl tertiary C-atoms was not included in the proposed mechanisms based on product analysis. The GC/MS data strongly indicated formation of Russell disproportionation products which retained the carbon backbone of the precursor. At the same time, tertiary RO_2 radicals are not readily converted into stable end-products, particularly carbonyls, without rearrangement or fragmentation.

The same conclusions were presented by Ceacero-Vega et al.[5], who analyzed OH reaction with menthol, borneol and fenchol in the gas-phase, as none of the reaction pathways proposed in their work include H-atom abstraction from alkyl tertiary C-atoms. As stated by the authors:

"*The SAR method predicts that ~15% of the attack of OH occurs at the other tertiary hydrogen site in both borneol and fenchol; however, no experimental evidence has been reported for this pathway. Attack at the second tertiary H-atom will probably lead to ring opened products, but they have not been detected*."

These conclusions are in very good agreement with our results. At the same time, please note that for all terpenoic alcohols, OH attacks the tertiary C-atoms in the α-position of the -OH moiety, resulting in its conversion into a carbonyl following elimination of HO_2.

Changes in the manuscript:

Section 2.6 was added, describing the SAR model used to derive total and partial $k_{OH_{aq}}$ values for fenchol, borneol, and menthol, and the major products of their reaction with OH.

Section 3 was rearranged; product analysis is now discussed in section 3.1.

A new section 3.2 was added as suggested by Referee 1, discussing general mechanisms and reasoning behind proposing specific reaction pathways. SAR figure for TAs was moved from the SI into section 3.2. The factors affecting the intramolecular selectivity of OH and its interplay with carbon order are now discussed in section 3.2. The rationale behind selecting the specific pathways and general mechanisms of TAs reaction with OH is also discussed in the newly added section 3.2.

Tables S4-S6 were added in the SI, with SAR data for all products included in Schemes 1-7.

The mechanisms are now discussed in subsections 3.2.1-3.2.3, which were adequately shortened. All reaction schemes were revised to showcase the most probable/major H-atom abstraction sites. The discussion in sections 3.2.1-3.2.3 was revised accordingly to justify the selection of specific pathways and discuss the contribution of other pathways. In most cases, however, SAR did not indicate the dominance of a specific H-atom abstraction site. As such, all possible pathways were not included in the reaction schemes, which is now clarified in section 3.2.

- For the formation of camphoric acid, the authors present a formation pathway. Shouldn't there be a closed-shell intermediate product after the β-scission?

Author's response: We agree that a key step in this reaction pathway was omitted.

Changes in the manuscript: A stable by-product, B15, was added after the β-scission in pathway I in scheme 4.

- As detailed in section 2.4, some of the quantifications were done by authentic standards, some by surrogate standards and some by fitting of the kinetic model to the experimental results. As this approach might be useful in specific cases it also opens the question how reliable the results are. If the fitted model results are used for that purpose, the model input directly influence the result. The authors

should clearly describe, what assumptions they used and how the quantification was done in detail. At the very least, all compounds that were quantified by model results should be clearly marked. Otherwise, the prominent claim of almost achieved mass-closure should be toned down a bit.

Author's response: We agree that the description of product identification, quantification, and the modeling lacked necessary detail. At the same time, please note that quantification methods, analysis conditions, standards used to quantify the products of OH reaction with terpenoic alcohols, concentrations of standards used to prepare the calibration curves, and linear coefficients of determination (R^2) values for each standard are all provided in the electronic supplement.

Changes in the manuscript: Section 2.4 (now section 2.5) was revised and expanded to include more details about the identification and quantification methods used. The reader is now directed to Tables S1- S3 in this section, which report quantitative parameters. Typographic errors in exponent values (concentration ranges) in Tables S1 – S3 were also corrected.

Likewise, the kinetic model section (now section 2.7) was revised and expanded to include a much more detailed description of model development. Moreover, a more detailed discussion about uncertainty connected with the use of authentic and surrogate standards was added in section 2.9.

"The uncertainty associated with the use of authentic standards was derived as 2σ values from triplicate experiments and usually did not exceed 10%. At the same time, the use of surrogate standards introduces a significantly higher uncertainty. However, because the yields initially obtained using surrogate standards were further adjusted based on experimental data, a 30% uncertainty was imposed on all product yields lacking authentic standards; this value was increased to 50% for the yields derived only from kinetic models (section 2.7)."

The molar yields in Tables S16 and S17 were adjusted accordingly, and the yields derived with authentic and surrogate standards and those derived from the model are now clearly marked, as suggested by the Referee. Likewise, the discussion on mass-closure and yields of $_{aq}$SOAs in the abstract, sections 3.3 and 4, was revised accordingly, to include uncertainties arising from the use of surrogate standards.

Moreover, the uncertainty values in Table 1 in the main text as well as in Tables S16 and S17 and the discussion connected with these tables were all adjusted accordingly.

- The introduction should be clearer structured, the authors jump from VOC to SOA formation back to VOC estimated emissions.

Author's response: We agree with this comment.

Changes in the manuscript: Section 1 was expanded, thoroughly revised and restructured as suggested by both referees – please see also the comments on the introduction provided by Reviewer 1. More transitional and introductory sentences were added.

The new introduction structure is as follows: general information about SOAs, atmospheric concentrations of SOAs and emission fluxes of SOAs precursors, including monoterpenes, oxygenated monoterpenoids and terpenoic alcohols, followed by emission sources of terpenoic alcohols and their emission fluxes. Then, commercial uses of terpenoic alcohols are discussed, and their relevance for indoor air chemistry and particle formation. Afterward, SOA formation mechanisms are discussed, including gas and aqueous SOAs, pointing out the knowledge gaps in $_{aq}$SOAs formation from monoterpenoids and terpenoic alcohols.

The aim of this work section at the end of the introduction was also expanded to better justify the selection of fenchol, borneol, and menthol as model precursors, considering their atmospheric abundance and structural features, representative of other primary and secondary monoterpenoids.

The following additional references were added, reporting emission fluxes, sources, atmospheric concentrations, and SOA yields and formation mechanisms from monoterpenoids and TAs, as well as supporting atmospheric relevance and representativeness of the investigated terpenoic alcohols:

Matasyoh et al., 2007; Fares et al., 2011; Kim et al., 2010; Joutsensaari et al., 2015; Yuan et al., 2025; Kivimäenpää et al., 2016; Mckinney et al., 2011; Li et al., 2020; Fares et al., 2012; Dickinson et al., 2022; Kelley et al., 2025; Abatzoglou et al., 2025; Bhatia and Letizia and Api, 2008; Bhatia et al., 2008; Shakil et al., 2026; Klein et al., 2016; Singer et al., 2006; Angulo Milhem et al., 2021; Rosales et al., 2022; Mellouki and Wallington and Chen, 2015; Wang et al., 2024b; Ceacero-Vega et al., 2012; Mehra et al., 2020; Wu et al., 2024; Amorim et al., 2020; Witkowski et al., 2023; Bleier and Elrod, 2013; Lai et al., 2025; Sander, 2023; Jenkin, 2004; Glasius et al., 2000.

- In line 71 it is stated that organic oxidation leads to new particle formation and it sounds as if that is the main fate of organics. I would suggest to restructure and if at all, mention NPF from organics as current topic of research that might occur in specific cases.

Author's response: We agree with the reviewer that the original wording could overemphasize new particle formation as the main fate of oxidized organics.

Changes in the manuscript: The wording of this sentence was changed from the original:

"In addition to producing new particles, the multiphase reactions of SOAs also alter physicochemical characteristics of OAs, including composition, optical and toxicological properties, and CCN and IN activity"

to

"In addition to affecting SOAs formation and processing, the multiphase chemistry alters physicochemical characteristics of OAs, including composition, optical and toxicological properties, as well as CCN and IN activity"

Furthermore, all mentions of organic nucleation were removed from the introduction.

- For the case of Menthol in scheme 6 and the table S10 not all products are listed with the respective ions. This makes it hard to judge the scientific soundness of the presented results in the scheme.

Author's response: Please note that, as detailed in section 2.5, quantitative analyses were conducted with GC-EI/MS and identification of non-acidic products was performed by GC-NCI/MS. As such, Tables S1-S3 in the revised supplement only contain data on quantified products. All products of the menthol + OH reaction shown in Scheme 6 were detected with GC-NCI/MS, as presented in the chromatograms in Fig. S2. Analogous results were obtained for borneol and fenchol. Also, GC-NCI/MS is not really well suited for quantitative analyses due to very large differences in response factors between analytes, even for relatively similar molecules [6].

Changes in the manuscript: A clarification was added at the beginning of section 3.1:

"The acquired chromatographic and mass spectrometric data were then used to propose the structures and formation pathways of the detected products, as detailed in sections 2.5 and 2.7. Products of R1-R3 were analyzed with GC/MS-EI, GC/MS-NCI (section 2.4.1), and LC-ESI/ToF/MS (section 2.4.2). In addition to qualitative data, some products were quantified with GC/MS-EI (Tables S1-S3). At the same time, molecular masses of products of R1-R3, and further structural characteristics, were obtained from GC/MS-NCI measurements, due to a much lower degree of fragmentation in this ionization mode.,,

- L 339 I am not sure how well partial rate coefficients can fit to yields as both parameters are very different

Author's response: We compare the partial $k_{OH_{aq}}$ values with the product yields under the assumption that products formed via the major pathways (identified by the higher values of partial rate coefficients) are formed in higher yields. Connecting the predicted intramolecular selectivity of an

oxidant with the product distribution is common in discussing mechanisms of gas and aqueous OH reactions with organic molecules [7]. For instance, Minakata and von Gunten stated that:

"Site- or moiety-specific reactivity determines the initial branching of aqueous oxidation and therefore constrains the expected transformation-product distribution."

Also, Mellouki et al. discuss group rate constants in connection with the distribution of products and branching ratios:

"the possible sites of attack … and hence the likely product distribution yields."

A further analysis is provided by the authors for different organics.

Finally, a comparison of product yields and partial rate coefficients predicted with the gas-phase SAR was presented by Ceacero-Vega et al. in a discussion on product yields from gas-phase reactions of menthol, borneol, fenchol, camphor, and fenchone with OH [5].

Changes in the manuscript: A clarification was added in section 3.2:

"Because partial $k_{OH_{aq}}$ derived with SAR represent the relative contributions of the H-atom abstraction site, their values provide information on reaction pathways and thus distribution of products [7, 8]."

A discussion in on product yields in section 3.3 was also revised:

"These data indicate that in the gas phase, H—atom abstraction from the —OH moiety at the α-position was the main reaction pathway for the cyclic alcohols listed in Table 2 [9]. This conclusion is also supported by the partial $k_{OH_{gas}}$ values estimated with SAR [5], indicating that H-atom abstraction in the α-position of —OH is a major reaction channel (ca. 60%) for cyclic alcohols, consistent with the measured yields of corresponding ketones [5]."

Minor comments:

References in the text are often just added to the sentence (Lines 154;169; 214; 220; 270 aso.) I would suggest to include them in the respective sentence to make the relation clear. Especially in Line 297 it is not clear if the reference is to the scheme in the respective publication or in this manuscript

Author's response: We agree with this comment.

Changes in the manuscript: The placement of references, including literature citations, figures and tables, was revised to improve the clarity of the presented discussion.

The tables in the SI are not in the same order as the schemes in the manuscript which makes it hard to follow.

Author's response: We agree with this comment.

Changes in the manuscript: The SI was revised and rearranged following the comments provided by both Referees. The Tables and figures order in the SI corresponds to the order of their appearance in the main text. We believe this to be an optimal solution for supporting the discussion in the main text.

L 264. There should be no hyphen before HO2

Author's response: We agree with this comment.

Changes in the manuscript: This line was corrected and, the use of hyphens in the text was reviewed.

L269 feasible does not seem to be the right adjective as it describes if something is possible to do, not to occur

Author's response: We agree with this comment.

Changes in the manuscript: The wording of this statement was revised, and the word "feasible" was removed from this line.

Scheme 6: the product from reaction path II has a methyl group instead of the hydroxylgroup.

Author's response: We agree with this comment.

Changes in the manuscript: The molecular structure of this product was corrected.

Table 1 subscripted text seems incomplete. I would not use 'neutrals' for the non-acidic compounds

Author's response: We agree with this comment.

Changes in the manuscript: The use of "neutral", referring to products without carboxylic moieties, was replaced with "non-acidic" throughout the manuscript.

SI line 14 it seems the references to the tables are wrong

Author's response: We agree with this comment.

Changes in the manuscript: Following revisions in the main text and the SI, tables and figures numbering was thoroughly revised.

SI Figure S6 the caption states that partial rate coefficients are shown, but the axis shows a relative reactivity, which is not a rate. Furthermore, the conditions for that prediction should be stated.

Author's response: We agree with this comment.

Changes in the manuscript: This figure was moved to the main text and is now discussed in more detail in newly added section 3.2. Furthermore, SAR section 2.6 was added in the main text, reporting the model parameters and detailing how the partial rate coefficients were predicted. The relative-reactivity figure was moved from the SI to the main text and is now presented as Figure 5. In addition, a new Figure 2 was added with an example of deriving $k_{OH_{aq}}$ values using SAR for norborneol; a terpenoic alcohol with fused C5 and C6 rings.

References

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