

Response to Referee Comment RC1:

Comments from the authors are in *italic*. Modifications in the text are marked in blue.

General comments:

The authors have provided a comprehensive experimental study of the reactions of sabinene with OH and O₃. The novel contributions include measuring the temperature dependence of the OH reaction and analyzing the chemical budget for OH radicals. The authors take pains to present previous work, describe their experimental and data analysis methods, and compare their results with past experimental and theoretical values. Based on the scientific significance and quality, I recommend accepting the manuscript.

We thank the reviewer for the valuable comments. They help to improve the manuscript and enrich the discussion of the ozonolysis mechanism.

Specific comments:

*The authors may want to consider other ozonolysis reaction pathways that may affect OH yield. This includes decomposition of chemically activated CH₂OO that produces OH (see Pfeifle et al., J. Chem. Phys. **2018**, 148, 174306) and rearrangements of vinyl hydroperoxides that may reduce OH yield (see Barber et al., J. Am. Chem. Soc. **2018**, 140, 10866-10880).*

Authors Response:

Additional discussion on the reaction pathway that may affect the OH yield is now included, which includes the small additional OH production (3 %) from the dissociation of CH₂OO. The rearrangement of vinyl hydroperoxides could be an explanation to reduce the OH yield expected from the mechanism. Figure 8 is added to illustrate the additional pathway of vinyl hydroperoxides.

L562-579:

“The OH yield from the ozonolysis reaction of sabinene of (26±29) % determined in the experiments is lower than the yield of 44 % expected from the mechanism in Wang and Wang (2017), but still within agreement due to the uncertainties presented in the experiment and the theoretical calculation. The OH yield is derived from the fraction of Criegee intermediate CI-1 that undergoes unimolecular decomposition forming an OH radical and an β-oxo alkyl radical (Fig. 2). ... The OH radical could reorientate and then recombine with the β-oxo alkyl radical, which would result in the production of 2-hydroxylketone (Barber et al., 2018; Kuwata et al., 2018, Fig. 8). With this additional mechanism, the theoretical OH yield of the ozonolysis of sabinene can be reduced. Though further investigation on the relative importance of the recombination pathway to the dissociation pathway is needed.”

The authors mention a significant discrepancy between their measured sabinene + O₃ rate constant and the SAR value from Jenkin. Some additional discussion of the possible origin of this discrepancy would be illuminating.

Authors Response:

Additional discussion of the possible origin of the discrepancy is now included.

L413-417:

“The large difference between the sabinene ozonolysis rate constants $k_{\text{SAB}+\text{O}_3}$ determined experimentally and from the SAR developed by Jenkin et al. (2020) is likely related to the ring strain of the bicyclic ring. Species in that SAR with ozonolysis rate constants differing by more than a factor of three are mostly polycyclic compounds (e.g., camphene, α -copaene, and 3-carene) including sabinene. Since the SAR was constructed mostly with acyclic and monocyclic alkenes, it is likely that impacts of ring strain on the ozonolysis rate constant for polycyclic species cannot be properly captured.”

Technical corrections:

It would be helpful if the authors briefly summarized the theoretical methods employed by Wang and Wang. This would give the reader some sense of how reliable the theoretical predictions are without having to look up the references.

Authors Response:

Brief descriptions of the theoretical method employed by Wang and Wang are now included in the manuscript.

L72-77:

“In the theoretical calculations conducted by Wang and Wang (2017 and 2018), molecular structures were first optimized and the vibrational frequencies were calculated at M06-2X/6-311++G(2df,2p) level. Electronic energies were calculated by wave function (UCBS-QB3) for the OH-oxidation of sabinene and at the RHF-UCCSD(T)-F12a level for the sabinene ozonolysis reaction. High-pressure limit rate constants were determined using the canonical transition state theory, whereas fast unimolecular reactions and their dependence on pressure and temperature were calculated with master equations (RRKM-ME) using Mesmer and MultiWell-2017 codes.”

There may be a few too many details presented in Section 3.3.

Authors Response:

Details regarding to the measurement of O₃, NO, NO₂, and photolysis frequencies are now removed from the text.

L194-197

“Concentrations of trace gas (O₃, NO, NO₂, VOCs) and radical species (OH, HO₂, RO₂), photolysis frequencies (Bohn et al., 2005; Bohn and Zilken, 2005), and OH reactivity were measured in the chamber experiments in this work.

The set of instruments used is listed in Table 1. Only the descriptions of measurements of species and quantity of interest (radicals, OH reactivity, and VOCs) in this study are included below.”

*The LIF instrument, since its 1σ uncertainty is smaller than that of the DOAS instrument, has the **higher** precision (contrary to line 207). Along similar lines, the relevant column heading in Table 1 is better termed **uncertainty** than **precision**.*

Authors Response:

Sentence 207 is now corrected that the LIF instrument has a higher precision than the DOAS instrument.

We prefer to use the term ‘precision’ to describe the fluctuation of measured values (i.e., statistical error), as ‘uncertainty’ was already used to describe the potential systematic error caused by the method of analysis (e.g., measurement of sabineketone in L247)

L219-221

“OH concentrations measured by the LIF instrument were used for the analysis of the ozonolysis experiments due to the higher time resolution and precision compared to that by the DOAS instrument.”

There are a few typographical errors to correct.

Authors Response:

Several typographical errors were found and corrected. The corrected typos were underlined.

L241-242:

“DOAS measurements were used for the analysis on that day as the CRDS method requires correction factors, whereas the DOAS method directly gives concentration values (Glowania et al., 2021).”

L22-23:

“In the ozonolysis experiments, the analysis of product measurements results in an acetone yield of (5 ± 2) %, a formaldehyde yield of (48 ± 15) %, a sabinaketone yield of (31 ± 15) %, and an OH radical yield of (26 ± 29) %.”

L26-28:

“The analysis reveals that the destruction rate of OH radical matches the production rate of OH suggesting that there is no significant missing OH source for example from isomerization reactions of peroxy radicals for the experimental conditions in this work.”

L134-137:

“In a temperature-controlled flow tube, OH radicals are generated in situ by photolysis of O_3 using laser pulses of a quadrupled Nd:YAG laser at a wavelength of 266 nm and a low pulse repetition rate of 1 Hz. $O(^1D)$ atoms produced from the photolysis of O_3 react with water vapor present in the gas mixture to produce OH radicals. Air containing a well-known concentration of sabinene is continuously passed through the flow tube.”