

Response to Referee Comment RC2:

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

We thank the reviewer for the valuable comments. They help to improve the manuscript.

**Referee Comment 1 – 2:**

- *Rate coefficient preferred over rate constant, although the latter is used in common parlance.*
- *Bimolecular rather than Bi-Molecular (and elsewhere), you have unimolecular already without a hyphen.*

**Authors Response 1 – 2:**

The text was modified accordingly, ‘rate constant’ is replaced with ‘rate coefficient’ and ‘bi-molecular’ is replaced with ‘bimolecular’.

**Referee Comment 3:**

*Are there plans to use a model to calculate the radical levels, or products? Will a mechanism for sabinene oxidation be developed to extend for example the MCM?*

**Authors Response 3:**

In the future it might be possible to develop a complete oxidation mechanism for sabinene including the formation of radicals.

At this stage of the study, however, the information from our experiments for specific product species is not complete enough to compare our results to model simulations. For example, RO<sub>2</sub> measurements in our study only give the total RO<sub>2</sub> concentrations but not speciated RO<sub>2</sub> concentrations.

**Referee Comment 4 – 9:**

- *Line (L) 13.  $\exp((575\pm 30)T-1)$  would be better as  $\exp((575\pm 30)/T)$ , also on L390, and elsewhere (e.g. Table 4).*
- *... the analysis of (not if)*
- *O<sub>3</sub> (Wang and Wang, 2017), ..... add respectively*
- *temperatures rather than temperature*

- *In situ and not in-situ*

#### **Authors Response 4 – 9:**

The text was modified accordingly following the order above in

- L13, L420, L431 (Table 4), L631
- L22
- L71
- L132
- L134

#### **Referee Comment 10:**

*L128, it is probably worth adding followed by reaction of the O(1D) atoms generated with water vapour present in the gas mixture.*

#### **Authors Response 10:**

The text was modified accordingly.

L136: “In a temperature-controlled flow tube ... O(<sup>1</sup>D) atoms produced from the photolysis of O<sub>3</sub> react with water vapor present in the gas mixture to produce OH radicals.”

#### **Referee Comment 11:**

*L138 Sabinene is measured using a TOC instrument with detection of the CO<sub>2</sub> formed after pyrolysis. Is there good evidence that 100% of the sabinene is removed to form CO<sub>2</sub>? Also, is the reason why a TOC is used for the high time-resolution required? It may be that the time-resolution is not good enough for the experiments for other methods (e.g. MS) – but perhaps a note to note this is needed.*

#### **Authors Response 11:**

We have good evidence that sabinene was quantitatively converted to CO<sub>2</sub>, as this method was also applied to other VOCs (alkanes, aromatics, monoterpenes) to measure their OH-reaction rate coefficients. Rate coefficients of the OH-oxidation reaction of these VOCs agree well with values recommended by IUPAC, suggesting that the VOC concentrations were accurately measured by the TOC method. Therefore, we are confident in the quantification of the VOCs concentration in the canister using the TOC method. Additional description is included in the text:

L149-153: “The catalytic conversion from VOCs to CO<sub>2</sub> was tested with other VOCs (alkanes, aromatics and monoterpenes) and showed a complete conversion. Therefore, it can be assumed that sabinene was completely converted to CO<sub>2</sub> during the TOC measurement. Assuming that all carbon stems from sabinene, its concentration in the canister can be calculated from the measured CO<sub>2</sub> concentrations.”

A measurement with a GC would have been also an option to determine the sabinene concentration in the experiment. However, the accuracy of the CO<sub>2</sub> detection by the CRDS instrument is higher than that of sabinene detection by the GC instrument as there was no GC calibration standard for sabinene available.

**Referee Comment 12:**

*L144 and L148. Temperatures here are in Celsius, whereas in the abstract they are given in K. I suggest that the abstract retains K as given, but perhaps K in brackets after the T in Celsius might be useful to add. Otherwise it will be confusing as for equation (2) on line 158 the T here has to be in K.*

**Authors Response 12:**

The text was modified accordingly in

L146-148: “In this method, a small flow (500 sccm) from the canister flowed through a pre-oven at 760 °C (1033 K) and afterward over a palladium catalyst at 500 °C (773 K).”

L155 (283 K to 343 K), L160 (283 K to 343 K), and L171 (0.005 % at 293 K).

**Referee Comment 13:**

*Please state the zero reactivity of the OH reactivity instrument.*

**Authors Response 13:**

The zero reactivity was about 2 s<sup>-1</sup> to 3 s<sup>-1</sup>. The text was modified accordingly:

L163-166: “The OH reactivity of air with sabinene was subtracted by its corresponding zero reactivity ranging from 2 s<sup>-1</sup> to 3 s<sup>-1</sup>. The rate coefficient of the OH reaction was calculated by using the sabinene concentration in the canister ([SAB]<sub>0</sub>) and the dilution factor  $f_{dil}$  determined from the flow rates:”

**Referee Comment 14 – 15:**

- Replace -EAR-1 by -E<sub>A</sub>/R to be consistent with the equation
- Please provide a reference for the ROxLIF instrument.

### **Authors Response 14 – 15:**

The text was modified accordingly in

- L173
- L212 (Fuchs et al., 2011)

### **Referee Comment 16:**

*L200-201. Is the HO<sub>x</sub> cell the same as the second LIF cell where HO<sub>2</sub> is measured? Is the RO<sub>x</sub> cell the same as “another low-pressure LIF detection cell”. Make this clear if the case. as HO<sub>x</sub> and RO<sub>x</sub> cells are not defined at present*

### **Authors Response 16:**

The HO<sub>x</sub> cell is the same as the LIF cell where HO<sub>2</sub> is measured. The text was modified accordingly:

L202-215 “The LIF instrument consists of three measurement cells for the separate detection of OH, HO<sub>2</sub>, and RO<sub>2</sub> radicals ... Similarly, the RO<sub>2</sub> concentration is finally derived from the difference between the fluorescence signals obtained in the RO<sub>x</sub> and the HO<sub>x</sub> cells.”

### **Referee Comment 17:**

*L202-207. It is excellent that there are two independent in situ methods for measuring OH. This is unique to SAPHIR. However, the statement that the DOAS and LIF instruments agreed with each other is a bit confusing if the difference between the 2 instrument is similar to the concentration of OH during the experiments? This suggests a significant difference? I agree though that because the OH concentration is similar to or below the 1-sigma precision of the DOAS instrument, that actually only the LIF instrument value is used.*

### **Authors Response 17:**

We think that the agreement between OH concentrations measured by the DOAS and LIF instruments in the ozonolysis experiments is good as the absolute difference between the two values is small. However, if OH concentrations are close to the limit of detection of the instrument, the relative difference can become large. The text was rephrased as follow:

**L216-221:** “In three of the experiments, both the LIF and DOAS instruments were available. In the two ozonolysis experiments on 24 and 25 January 2022 (Table 5), mean OH concentrations measured by the DOAS and LIF instruments were both low at around 0 to  $1 \times 10^6 \text{ cm}^{-3}$  (Fig. 3 and Fig. S1). The mean value of the difference between OH concentrations measured by the two instruments was about  $0.7 \times 10^6 \text{ cm}^{-3}$ . This is close to the limit of detection of the DOAS instrument (**Error! Reference source not found.**). 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.”

**Referee Comment 18:**

*L212-213. DOAS is used for the OH measurements in the photooxidation experiments, and there is a note that the difference with LIF might be due to an unaccounted calibration error. Is there confidence then in the LIF value for the O<sub>3</sub> experiments when only the LIF value is used?*

**Authors Response 18:**

For the calculations of kinetic parameters from the ozonolysis experiment, we did not make use of OH concentration measurements. OH measurements by the LIF instrument in the ozonolysis experiment were only used to calculate the OH production rate during the experiment (Fig. 9). The overall small production rate of less than 1 ppbv/h and the low precision of OH measurements give a scatter of data points of approximately 50%. An additional uncertainty of 25% in the OH concentration values, would therefore not change any of the conclusions.

**Referee Comment 19:**

*Can a note be added about why the PTR was not calibrated for sabinene. Is there an experimental limitation which prevents this?*

**Authors Response 19:**

Unfortunately, there was no calibration standard available to accurately determine the sensitivity of the PTR-MS instrument for sabinene. The scaling of the ion mass signal to match the increase in the measured OH reactivity at the point of injection of a VOC has been proven to give an accurate estimate of the calibration factor of PTR instruments in previous chamber experiments if the OH reaction rate constant is known. In this work, the OH reaction rate constant was independently measured and therefore well known.

**Referee Comment 20:**

*factors not factorss*

**Authors Response 20:**

The text was modified accordingly in L242.

**Referee Comment 21:**

*There are quite a few Novelli et al., 2023 references (a, b, c, ....), and specific figures are referred to in these (which are Eurochamp datasets), e.g. from Table 2 and also in the text. The figures were all blank for me when I clicked on the links (the axes show but no line or point on the graphs). I wonder if the Supplementary Information (SI) for this paper could be used to display these specific figures instead of having to click on links (which did not any data for me) – it would be easier for the reader? I think if the intention of the references is to contain significant supporting data for each experiment, then this is fine (but the figures were blank for me), but if specific Figures from these databases are cited, then these ought to be more readily observable via the SI.*

**Authors Response 21:**

Time series of all trace gases and radicals from experiments in this work can be found in the figures of the main paper and in supplementary information. The reference to the EUROCHAMP database is only meant to link to the data but is not thought to give additional information. Unfortunately, there is indeed some problems with displaying time series properly on the webpage of the EUROCHAMP database.

**Referee Comment 22:**

*Figure 3. For the last panel, the loss of RO<sub>2</sub> seems to be completely dominated by RO<sub>2</sub>+HO<sub>2</sub>, with RO<sub>2</sub>+RO<sub>2</sub> being very small indeed. Given that the concentrations of RO<sub>2</sub> and HO<sub>2</sub> are similar (two other panels), then I think a comment is needed to say that the RO<sub>2</sub>+RO<sub>2</sub> rate coefficient is 20 times smaller than for RO<sub>2</sub>+HO<sub>2</sub> (this information is in the SI).*

**Authors Response 22:**

Additional information was added to the text to describe the fraction of RO<sub>2</sub> undergoing different bimolecular reaction pathways.

L263-266: “RO<sub>2</sub> radicals were expected to react exclusively with HO<sub>2</sub> radicals in the absence of NO, if only bimolecular reactions of RO<sub>2</sub> radicals are considered. The self-reaction between RO<sub>2</sub> radicals is expected to be of minor importance compared to the reaction with HO<sub>2</sub> radicals, as the reaction rate constant of self-reactions of RO<sub>2</sub> is about 20 times slower than that of the reaction with HO<sub>2</sub> radicals (Supplementary material Section 1).”

L283-286: “Over 80 % of RO<sub>2</sub> radicals were expected to react with NO and the remaining part mostly reacted with HO<sub>2</sub> radicals in the photooxidation experiments, if only bimolecular reactions of RO<sub>2</sub> radicals are considered. For the experiment on 06 July 2022, only around 60 % RO<sub>2</sub> radicals reacted with NO at the beginning due to the low NO concentration caused by cloudy weather.”

**Referee Comment 23 – 26:**

- *Add (100 ppmv) after CO to make this clearer again.*
- *The MCM is used to calculate photoylsis rates of ketones – can a reference please be given for this.*
- *Known and not know (~ L407)*
- *“OH production rate was excellently balanced”, better might be “.... “ the OH production was very well balanced...”*

**Authors Response 23 – 26:**

The text was modified accordingly in

- L294
- L321 (Atkinson et al. 2006)
- L407
- L608