

## Response to Community Comment CC1:

We thank the reviewer for the valuable comments and suggestions. The input has improved the manuscript. Comments from the authors are in *italic*. Modifications in the text are marked in blue.

### Comment 1:

*From Eq. 4 to Eq. 5, the concentrations of O<sub>3</sub> and OH are assumed constant. This is not a proper assumption. Fig 3 and Fig 4 showed the changes of concentrations. Because the concentrations of OH and O<sub>3</sub> are available from experimental measurements, it is probably better to simply integrate the concentrations as,*

$$\frac{d[SAB]}{[SAB]} = -(k_{O_3}[O_3]_t + k_{OH}[OH]_t + k_{dil})dt$$
$$\ln \frac{[SAB]_0}{[SAB]_t} = k_{O_3} \int_0^t [O_3]_{t'} dt' + \int_0^t [OH]_{t'} dt' + \int_0^t k_{dil} dt'$$

*Each integrate can be obtained from the experimental concentrations. A linear regression can be used to obtain  $k_{O_3}$  and  $k_{OH}$ , and contributions of OH and O<sub>3</sub> in degradation of sabinene can be obtained.*

### Response from authors for comment 1:

We thank the reviewer for the suggestion. The ozonolysis rate constant recalculated with the integration method resulted in value of  $(3.4 \pm 0.8) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ , which is similar to the value obtained from the regression method  $(3.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ .

However, the integration method is less robust than the regression method as it is more sensitive to the choice of reference sabinene concentrations  $[SAB]_0$ . For this reason and since the ozonolysis coefficients obtained agree within 9 %, we still prefer to use the regression method to calculate the OH yield of the ozonolysis reaction. As the time interval used for the calculation of the OH yield is short, the error of replacing the integrated O<sub>3</sub> concentration with its mean value will be smaller compared to the calculation of the rate coefficient.

The value of rate constant  $k_{SAB+OH}$  in the ozonolysis experiment (at a temperature of ~ 278K) is not calculated as the loss of sabinene was mostly from the ozonolysis reaction, therefore the uncertainty of  $k_{SAB+O_3}$  would lead to a very large uncertainty in  $k_{SAB+OH}$ . Values of the rate constant  $k_{SAB+OH}$  in the photooxidation experiments (at around 300K) were determined using a simplified chemical model, which is very similar to the integration method. The value obtained was then compared with the rate determined from the OH reactivity measurement in the laboratory.

The manuscript is modified accordingly:

L327-369:

“Solving the differential equation Eq. (3) yields the following expression:

$$\ln \frac{[\text{SAB}]_0}{[\text{SAB}]_t} = k_{\text{SAB}+\text{O}_3} \int_0^t [\text{O}_3]_{t'} dt' + k_{\text{SAB}+\text{OH}} \int_0^t [\text{OH}]_{t'} dt' + \int_0^t k_{\text{dil}} dt' \quad (1)$$

The reaction rate coefficient  $k_{\text{SAB}+\text{O}_3}$  is determined .... Using Eq. (7) to determine the OH yield by obtaining the regression coefficient  $k_{\text{loss}}$  is more robust than using Eq. (1) and calculates the OH yield for every timestep within the time interval of analysis, as regression is less sensitive to the choice of reference sabinene concentration  $[\text{SAB}]_0$ .”

L372-376:

“The rate coefficient  $k_{\text{SAB}+\text{OH}}$  was determined by minimizing the root-mean-square error between sabinene concentrations measured by the PTR-TOF-MS instrument and calculations using a simplified chemical model as described in Hantschke et al. (2021). The chemical model calculates the loss rate of sabinene with measured dilution rate, OH and O<sub>3</sub> concentrations with a time step of 1 minute. The simplified model only includes the chemical loss of sabinene by the reactions with OH and O<sub>3</sub> and by dilution, without other secondary chemistry.”

Values of  $k_{\text{SAB}+\text{O}_3}$  changed from  $(3.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$  to  $(3.4 \pm 0.8) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$  in

L16, L404, L630, Table 3, Table 4

### Comment 2:

*Table 5 Yields of Products: For reaction with OH, the yields from the theoretical study (Wang & Wang, 2018) assumed 100% yield of RO from reactions of ROO + NO. This is probably not correct. There should be a fraction of RONO2 formation.*

### Response from authors for comment 2:

The production of organic nitrates was overlooked in the calculation, the expected yield of formaldehyde and acetone should be lower than the values stated in Table 5. Using organic nitrate yields of (20 – 35) % usually applied for RO<sub>2</sub> radicals derived from the oxidation of monoterpenes (Rollins et al., 2010), and the OH-additional branching ratio of 47 %, we expect that the yields for HCHO and sabinaketone were about (31 – 38) %.

We also overlooked the unimolecular reaction for peroxy radical SABINOHBO2 when comparing the expected acetone yield based on Wang and Wang and the yield determined in the experiment. The expected acetone yield of 45 % stated on the manuscript only considers the branching ratio of the OH-

addition reaction, which does not consider the production of organic nitrate as mentioned, as well as the unimolecular reaction of peroxy radical SABINOHBO2 and the fraction of SABINOHBO2 that undergoes bimolecular reactions. The expected acetone yield after taking account into the unimolecular reaction rate for peroxy radical SABINOHBO2 of  $5 \text{ s}^{-1}$  in the photooxidation experiments should be around 4 %, which is lower than the experimental yield of about 20 %.

We removed the yield values derived from theoretical calculations presented in Table 5.

The manuscript is modified accordingly.

L506-512:

“In the OH oxidation mechanism by Wang and Wang (2018), HCHO is only produced from the subsequent chemistry of the RO<sub>2</sub> radical SABINOHBO2 that results from one of the two OH-addition reactions of sabinene (reaction pathway (a), Fig. 1). It is reasonable to expect that about 20 % to 35 % of RO<sub>2</sub> derived from the OH-oxidation of sabinene forms organic nitrates when it reacts with NO based on the study of peroxy radicals derived from monoterpenes oxidation (e.g., Rollins et al., 2010), Therefore, the HCHO expected from the OH-oxidation of sabinene should be 31 % to 38 % when considering the branching ratio of reaction pathway (a) stated in Wang and Wang (2018) and the organic nitrate yield. This agrees with the HCHO yield of (46±25) % (Table 5) determined in the photooxidation experiments.”

L515-519

“ ... SABINOHBO2 that undergoes an isomerization reaction or forms organic nitrates in the reaction with NO, from which eventually acetone is produced. For atmospheric conditions like in the experiments in this work, it is expected that more than 90 % of SABINOHBO2 undergoes the unimolecular reaction ( $k_{\text{uni}} \sim 5 \text{ s}^{-1}$ , Fig. 1) and less than 10 % undergoes bimolecular reactions ( $k_{\text{RO}_2} < 0.4 \text{ s}^{-1}$ , Fig. 4 and Figs. S2 and S3). Therefore, the acetone yield is expected to be only around 4 % (reaction path (b) in Fig. 1).”

L520

“The experimentally determined acetone yield of (21±15) % is significantly higher than this value.”

L535-537

“The sabinaketone yield of (19±16) % from the OH-oxidation of sabinene determined from the experiment is lower than the yield of 31 % to 38 % expected from the mechanism by Wang and Wang (2018) after taking account into the branching ratio of reaction pathway (b) in Fig. 1 and the potential production of organic nitrates.”

**Comment 3:**

*It should be noticed that the theoretical calculations all the time carry uncertainty. The predicted rate coefficients usually have uncertainty, about one order of magnitude when using ROCBS-QB3 energies. The results from theoretical calculations can be considered as the most probable values, or sometimes are biased. Therefore, experimentalists need to be aware of this, and theoreticians need to adjust the barrier heights to match the “reliable” experimental data, which are unfortunately rather limited and not available for most of time. Overall, I would consider reasonable agreement between the experimental measurements here and the previous theoretical calculations.*

**Response from authors for comment 3:**

We thank the reviewer for pointing out the uncertainties in the theoretical calculations. We assume the rate coefficient referred to here is the unimolecular rate constant for the RO<sub>2</sub> radical SABINOHBO<sub>2</sub> that can affect the acetone yield.

The manuscript is modified accordingly.

L520-534:

“The experimentally determined acetone yield of (21±15) % is significantly higher than this value. To bring both values into agreement, the rate constant of the unimolecular reaction of SABINOHBO<sub>2</sub> would need to be in the same order of magnitude as the loss rates constant of bi-molecular RO<sub>2</sub> reactions in this study (~0.2 s<sup>-1</sup>), so that about half of the RO<sub>2</sub> radical SABINOHBO<sub>2</sub> undergoes bi-molecular reactions (mainly with NO). The uncertainty of the unimolecular reaction rate coefficient calculated in Wang and Wang (2018) of about 5 s<sup>-1</sup> has an uncertainty of about one order of magnitude. Therefore, the unimolecular reaction rate constant calculated by Wang and Wang (2018) agrees with the rate constant required to reach a good agreement of acetone yield, despite the large difference between the acetone yield determined in the experiments and the yield expected from the mechanism in Wang and Wang (2018).

It should be noted that acetone might be produced from pathways other than the reaction pathways of RO<sub>2</sub> radical SABINOHBO<sub>2</sub> as suggested in Wang and Wang (2018). This would be consistent with the observation that the acetone yield found in this study and in Carrasco et al. (2006) does not strongly depend on the NO concentration (Table 5), which would be expected, if acetone is produced from reaction pathway without other competitions. For example, acetone might be produced from the bimolecular reactions of a RO<sub>2</sub> radical that does not have competing isomerization reactions, or could be produced from a very fast isomerization reaction that bimolecular reactions cannot compete with at typical NO concentrations in the atmosphere.”