Atmospheric photooxidation and ozonolysis of sabinene: Reaction rate constants, product yields and chemical budget of radicals

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1. Overview of trace gas concentration measurements in the experiments

The RO₂ loss rate constant to bimolecular reactions ($k_{\text{RO}_2}$) is calculated using measured trace gases and radical concentrations. The reciprocal of $k_{\text{RO}_2}$ give the chemical lifetime of RO₂ to losses from bimolecular reactions with typical reactants in the atmosphere.

\[ k_{\text{RO}_2} = k_{\text{RO}_2 + \text{HO}_2} [\text{HO}_2] + k_{\text{RO}_2 + \text{NO}} [\text{NO}] + k_{\text{RO}_2 + \text{RO}_2} [\text{RO}_2] \]  \hspace{1cm} (S1)

where $k_{\text{RO}_2 + \text{HO}_2}$, $k_{\text{RO}_2 + \text{NO}}$, and $k_{\text{RO}_2 + \text{RO}_2}$ are the reaction rate constants of RO₂ with HO₂, NO, and RO₂ respectively. The values are $k_{\text{RO}_2 + \text{HO}_2} = 2 \times 10^{-11}$, $k_{\text{RO}_2 + \text{NO}} = 9 \times 10^{-12}$, and $k_{\text{RO}_2 + \text{RO}_2} = 1 \times 10^{-12}$ cm³ s⁻¹ at 298 K, which are taken from SAR in Jenkins et al. (2019). The value of the RO₂ + RO₂ reaction of $1 \times 10^{-12}$ cm³ s⁻¹ is the upper limit of the reaction rate constant for the self-reaction of secondary and tertiary β-hydroxyl peroxy radicals with 10 carbon atoms, which are the peroxy radicals expected from the oxidation of sabinene by OH radicals.
Figure S1. Overview plots of measured radical and trace gas concentrations during the ozonolysis experiment performed on 25 January 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber and the red dotted line denotes when 200 ppmv of CO was injected.
Figure S2. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low NO mixing ratio performed on 30 June 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber.
Figure S3. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low NO mixing ratio performed on 06 July 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber.
Figure S4. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with medium NO mixing ratio performed on 06 September 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber. The plot of the RO$_2$ loss rate constant to bimolecular reactions, $k_{RO2}$, is not included in this experiment, as measurements of HO$_2$ and RO$_2$ were not available.
Figure S5. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low and medium NO mixing ratio performed on 08 September 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber. The plot of the RO$_2$ loss rate constant to bimolecular reactions, $k_{RO_2}$, is not included in this experiment, as measurements of HO$_2$ and RO$_2$ were not available.
2. Determination of the reaction rate constant $k_{\text{SAB}+\text{OH}}$

![Diagram showing modeled and measured sabinene concentrations](Figure S6.png)

**Figure S6.** Modelled and measured sabinene concentrations in the photooxidation experiment with medium NO mixing ratios (05 July 2022) used for the determination of the OH reaction rate constant $k_{\text{SAB}+\text{OH}}$. The red line and shaded area represent the simulation results applying a value of the OH reaction rate constant of sabinene of $k_{\text{SAB}+\text{OH}} = (1.4 \pm 0.5) \times 10^{-10}$ cm$^3$ s$^{-1}$. 
3. Determination of product yields from the oxidation of sabinene

![Graphs showing product yields from sabinene oxidation](image)

**Figure S7.** Yields of HCHO (a), acetone (b) and sabinaketone (c) from the photooxidation and ozonolysis of sabinene. The plots are similar to Figure 6 in the main paper, but all data points are included in the regression analysis. Value of the yield named ‘Photooxidation’ is the yield calculated from the data combining the photooxidation experiments with low and medium NO mixing ratios.
Table S1. Values of the rate constant of the loss of sabinene to chemical reactions, \( k_{\text{loss,chem}} \), determined in the ozonolysis experiments.

<table>
<thead>
<tr>
<th>OH scavenger</th>
<th>Experiments</th>
<th>( k_{\text{loss,chem}} / 10^{17} \text{ cm}^3 \text{ s}^{-1} ) (without corrections of the reaction ( \text{HO}_2 + \text{O}_3 ))</th>
<th>( k_{\text{loss,chem}} / 10^{17} \text{ cm}^3 \text{ s}^{-1} ) (with correction of the reaction ( \text{HO}_2 + \text{O}_3 ))</th>
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<tbody>
<tr>
<td>Yes</td>
<td>24 January 2022 2(^{nd}) injection</td>
<td>4.1±0.4</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>25 January 2022 3(^{rd}) injection</td>
<td>3.7±0.4</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>25 January 2022 4(^{th}) injection</td>
<td>3.3±0.3</td>
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<tr>
<td></td>
<td>Mean value (i.e., ( k_{\text{SAB+O}_3} ))</td>
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<tr>
<td>No</td>
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<td>4.4±0.6</td>
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<td>25 January 2022 2(^{nd}) injection</td>
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<td>Mean value</td>
<td>4.8±0.5</td>
<td>4.3±0.7</td>
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</tbody>
</table>

\( k_{\text{loss,chem}} \) (without CO) / \( k_{\text{loss,chem}} \) (with CO) 1.3±0.2 1.2±0.3

OH yield (30±22)% (18±25)%

References