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Atmospheric photooxidation and ozonolysis of sabinene: reaction rate coefficients, product yields, and chemical budget of radicals

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S1. Overview of trace gas concentration measurements in the experiments

The RO_2 loss rate coefficient to bimolecular reactions (k_{RO2}) is calculated using measured trace gases and radical concentrations. The reciprocal of k_{RO2} gives the chemical lifetime of RO_2 to losses from bimolecular reactions with typical reactants in the atmosphere.

$$k_{\mathrm{RO_2}} = k_{\mathrm{RO_2+HO_2}}[\mathrm{HO_2}] + k_{\mathrm{RO_2+NO}}[\mathrm{NO}] + k_{\mathrm{RO_2+RO_2}}[\mathrm{RO_2}] \quad \text{(S1)}$$

where $k_{RO2+HO2}$, k_{RO2+NO}, and $k_{RO2+RO2}$ are the reaction rate coefficients of RO_2 with HO_2, NO, and RO_2 respectively. The values are $k_{RO2+HO2} = 2\times10^{-11}$, $k_{RO2+NO} = 9\times10^{-12}$, and $k_{RO2+RO2} = 1\times10^{-12}$ cm^3 s^{-1} at 298 K, which are taken from SAR in Jenkins et al. (2019). The value of the RO_2 + RO_2 reaction of 1×10^{-12} cm^3 s^{-1} is the upper limit of the reaction rate coefficient 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.

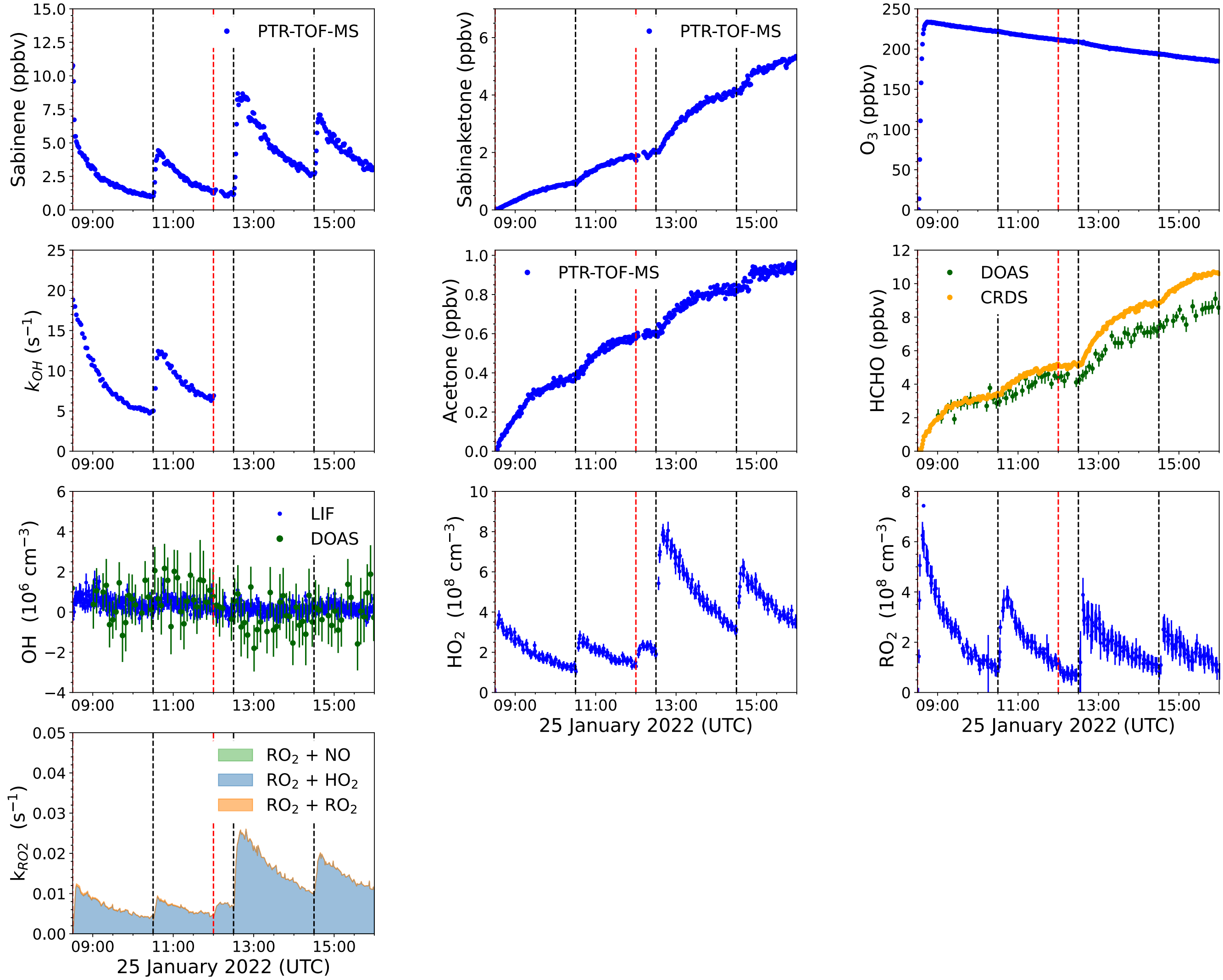

Figure S1. Overview plots of measured radical and trace gas concentrations during the ozonolysis experiment performed on 25 January 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber and the red dotted line denotes when 200 ppmv of CO was injected. After the injection of CO, the OH reactivity was too high to be measured (~1000 s^{-1}).

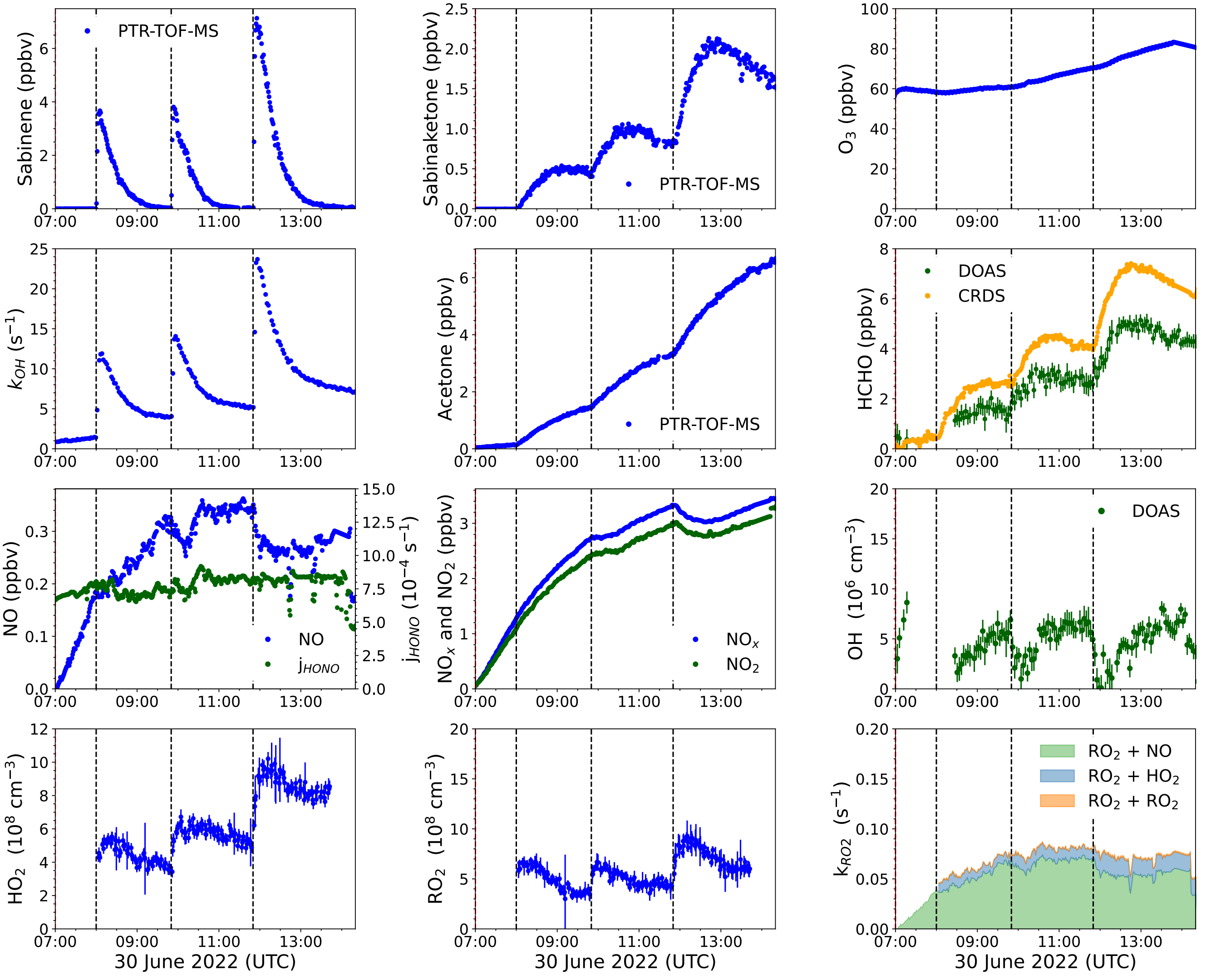

Figure S2. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low NO mixing ratio performed on 30 June 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber.

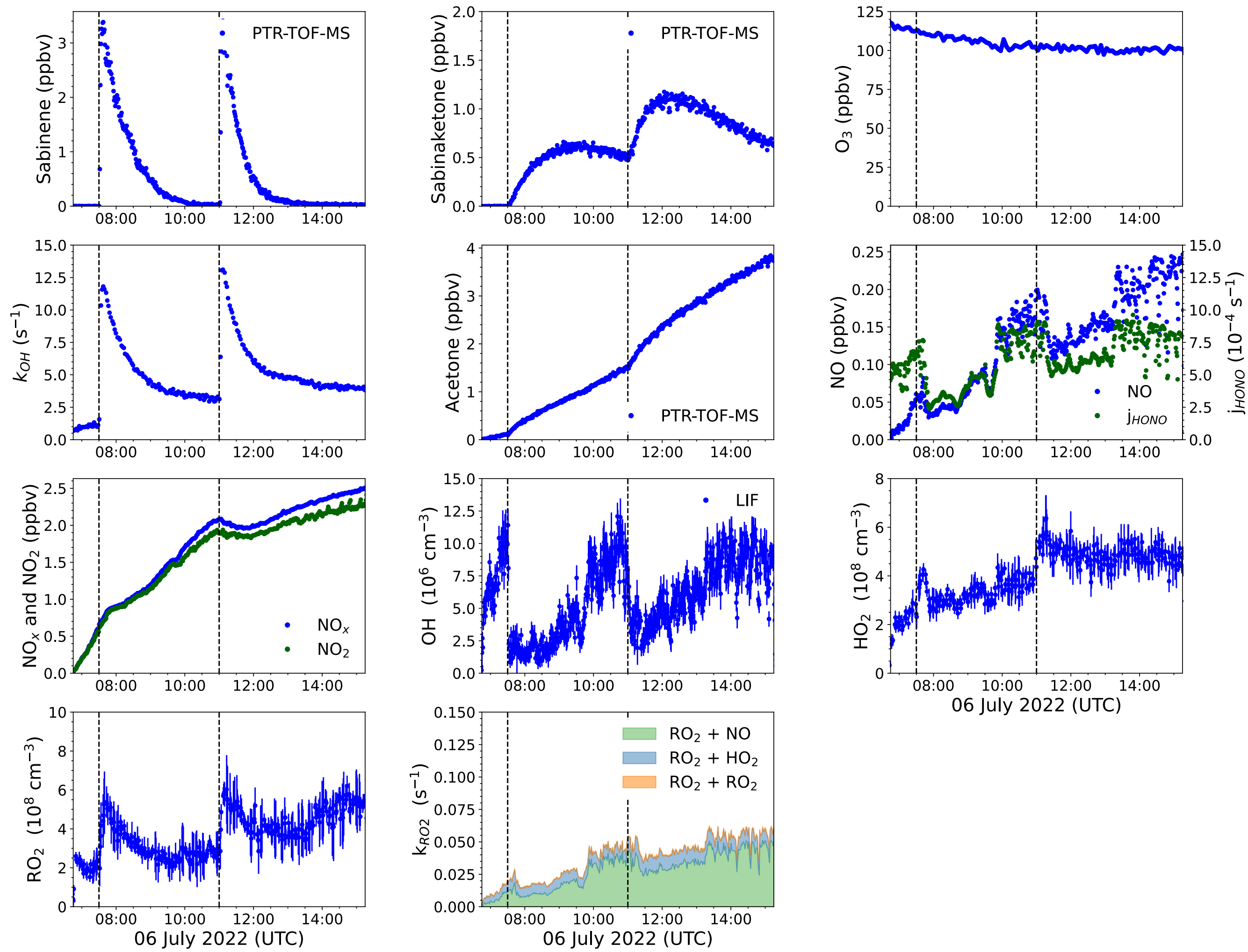

Figure S3. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low NO mixing ratio performed on 06 July 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber.

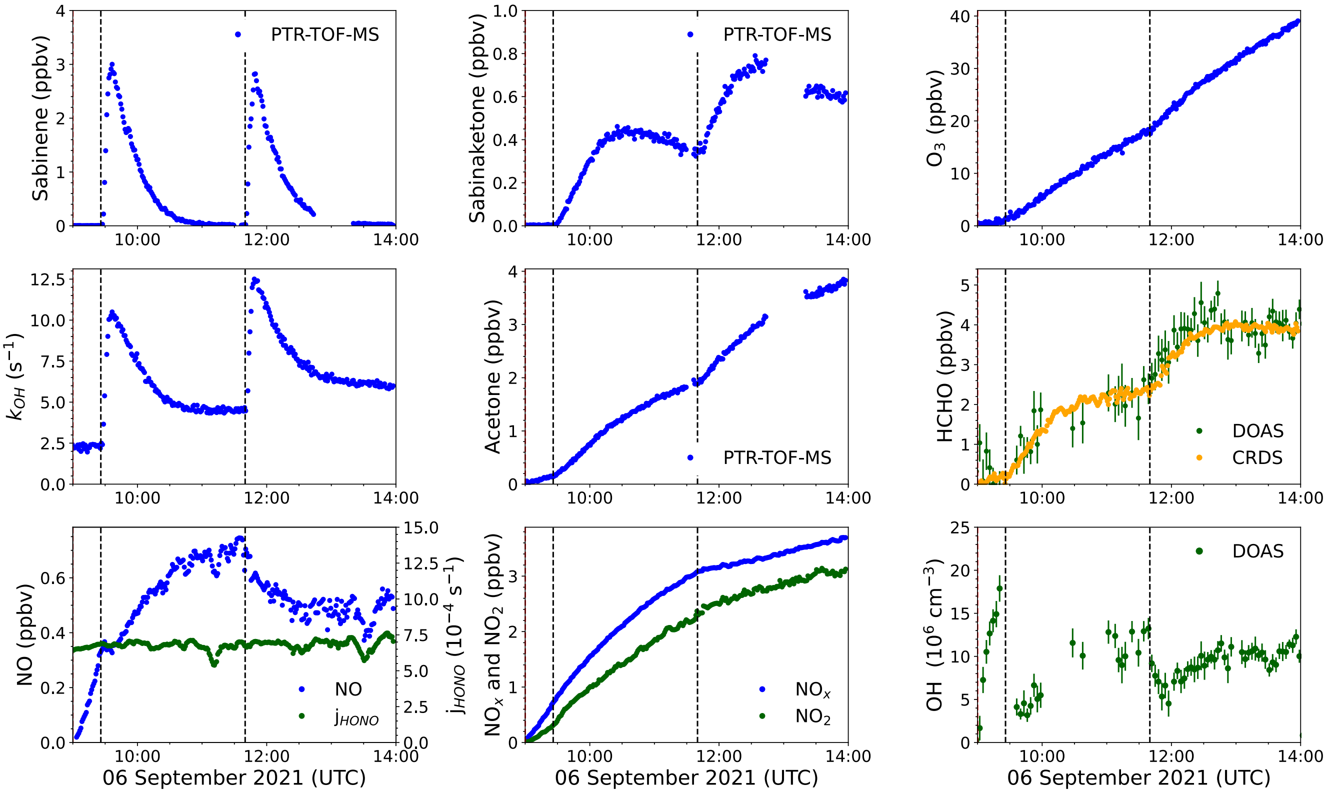

Figure S4. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with medium NO mixing ratio performed on 06 September 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber. The plot of the RO_2 loss rate coefficient to bimolecular reactions, k_{RO2}, is not included in this experiment, as measurements of HO_2 and RO_2 were not avaialble.

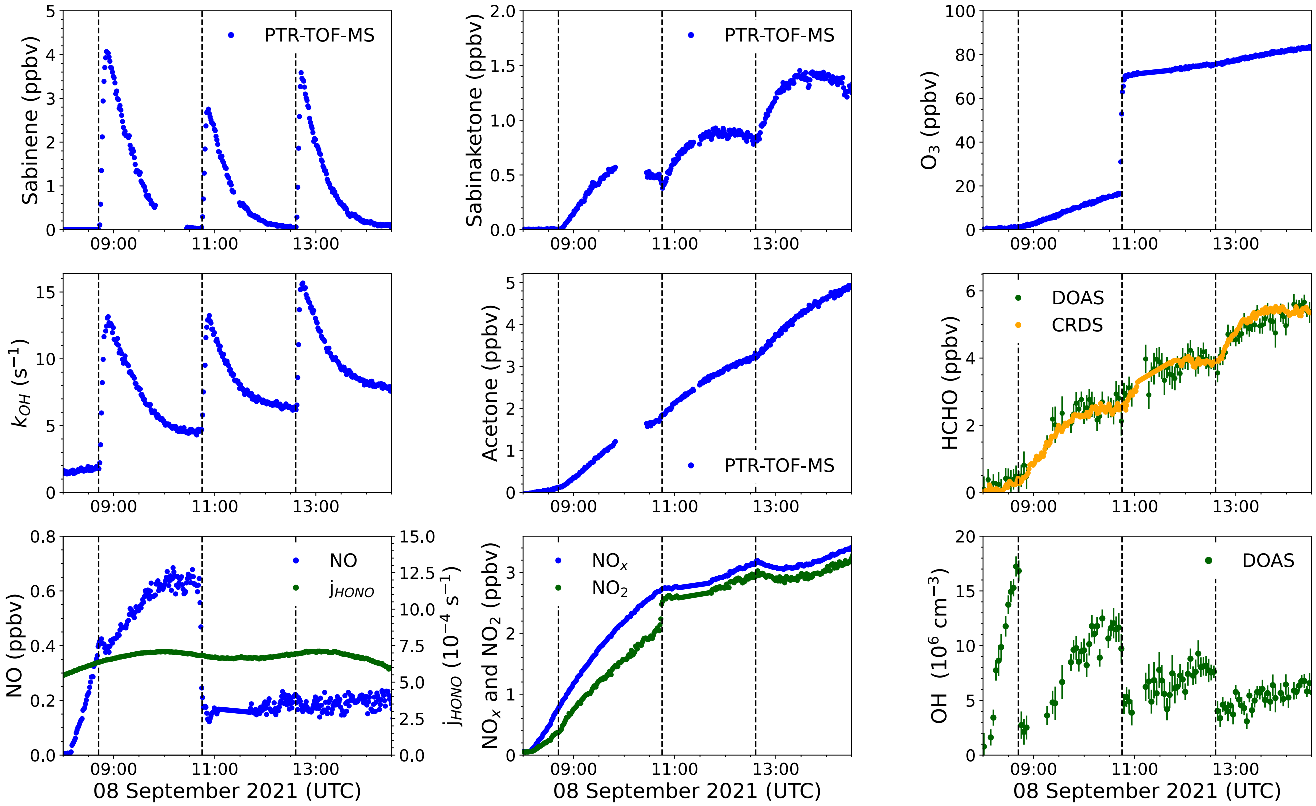

Figure S5. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low and medium NO mixing ratio performed on 08 September 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted lines denote when sabinene was injected into the chamber. The plot of the RO_2 loss rate coefficient to bimolecular reactions, k_{RO2}, is not included in this experiment, as measurements of HO_2 and RO_2 were not avaialble.

S2. Determination of the reaction rate coefficient k_{SAB+OH}

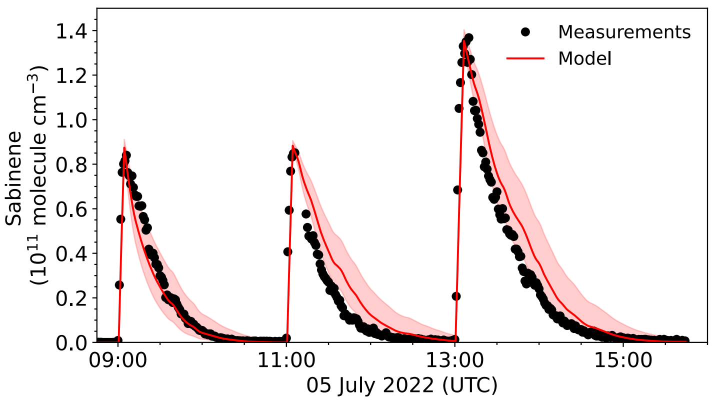

Figure S6. Modelled and measured sabinene concentrations in the photooxidation experiment with medium NO mixing ratios (05 July 2022) used for the determination of the OH reaction rate coefficient k_{SAB+OH}. The red line and shaded area represent the simulation results applying a value of the OH reaction rate coefficient of sabinene of $k_{SAB+OH} = (1.4\pm0.5)\times10^{-10}$ cm^3 s^{-1}.

S3. Determination of product yields from the oxidation of sabinene

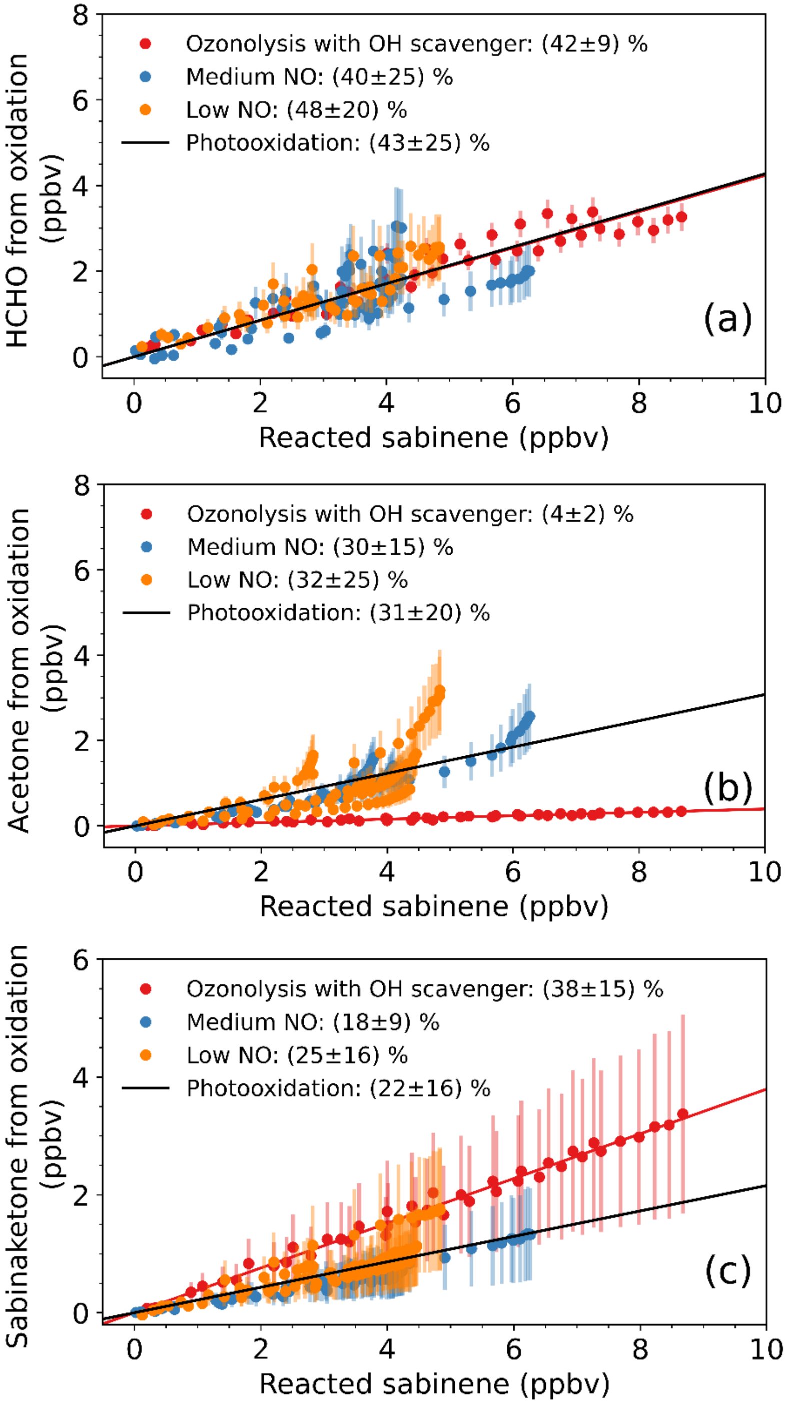

Figure S7. Yields of HCHO (a), acetone (b), and sabinaketone (c) from the photooxidation and ozonolysis of sabinene. The plots are similar to Figure 6 in the main paper, but all data points are included in the regression analysis. The value of the yield named ‘Photooxidation is the yield calculated from the data combining the photooxidation experiments with low and medium NO mixing ratios.

Table S1. Values of the rate loss coefficient of sabinene to chemical reactions determined in the ozonolysis experiments, after correcting to the loss to dilution and the production of OH from the reaction of HO_2+O_3.

Experiments	$k_{SAB+O3}\times(1+\gamma_{SAB})$ / 10^{-17} cm^3 s^{-1} (without corrections of the reaction HO_2+O_3)	$k_{SAB+O3}\times(1+\gamma_{SAB})$ / 10^{-17} cm^3 s^{-1} (with correction of the reaction HO_2 + O_3)
24 January 2022 1st injection	4.8±0.4	4.4±0.6
25 January 2022 1st injection	5.5±0.6	4.9±0.8
25 January 2022 2nd injection	4.4±0.4	3.9±0.6
Mean value	4.8±0.5	4.3±0.7
$k_{SAB+O3}\times(1+\gamma_{SAB})$ / (k_{SAB+O3})	1.4±0.3	1.3±0.3
OH yield	(41±26)%	(26±29)%

References

Jenkin, M. E., Valorso, R., Aumont, B., and Rickard, A. R.: Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction, Atmos. Chem. Phys., 19, 7691–7717, https://doi.org/10.5194/acp-19-7691-2019, 2019.