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 RO_2 loss rate constant to bimolecular reactions (k_{RO2}) is calculated using measured trace gases and radical concentrations. The reciprocal of k_{RO2} give 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 constants 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 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.

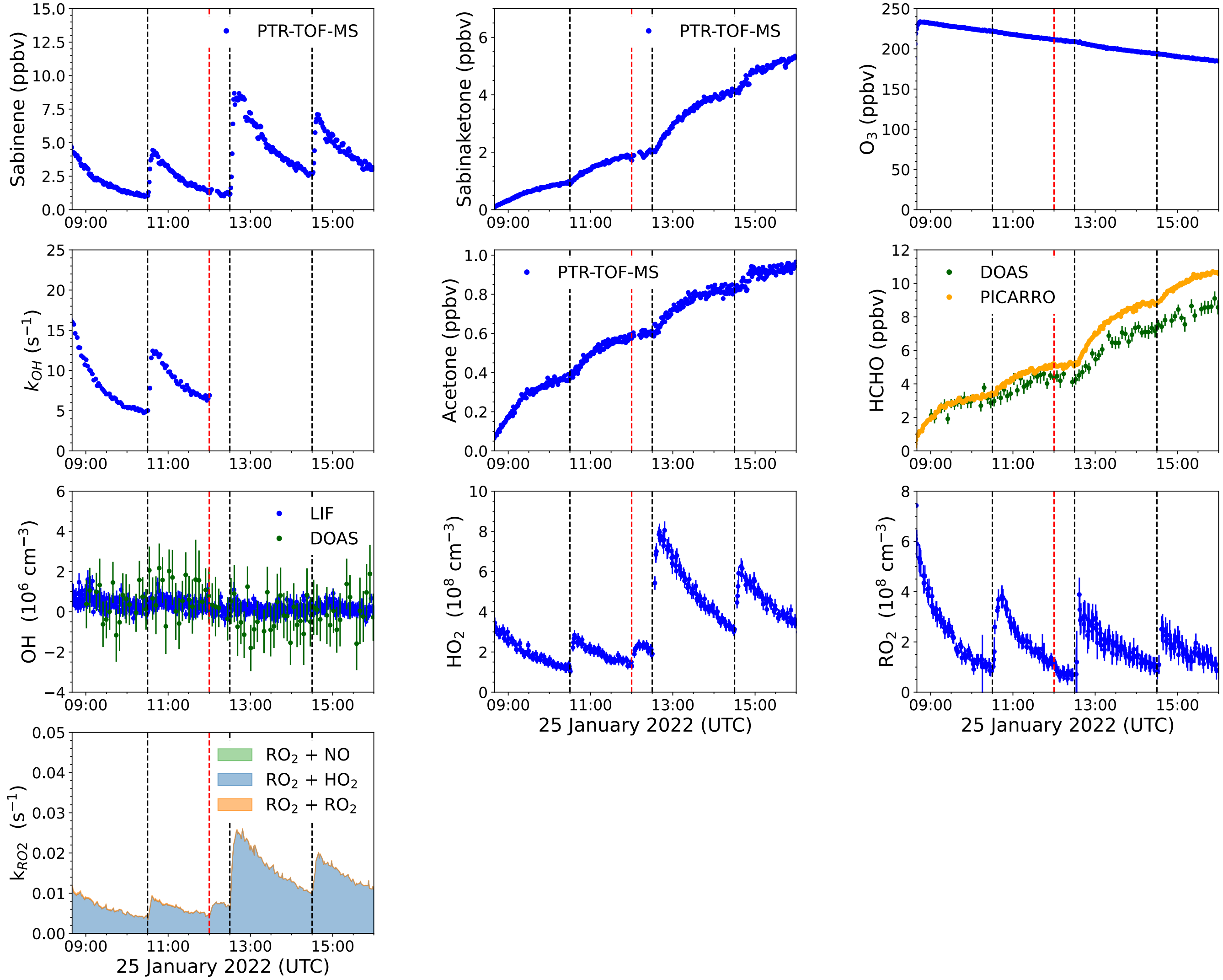

Figure S1. Overview plots of measured radical and trace gas concentrations during the ozonolysis experiment performed on 25 January 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection. The black dotted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

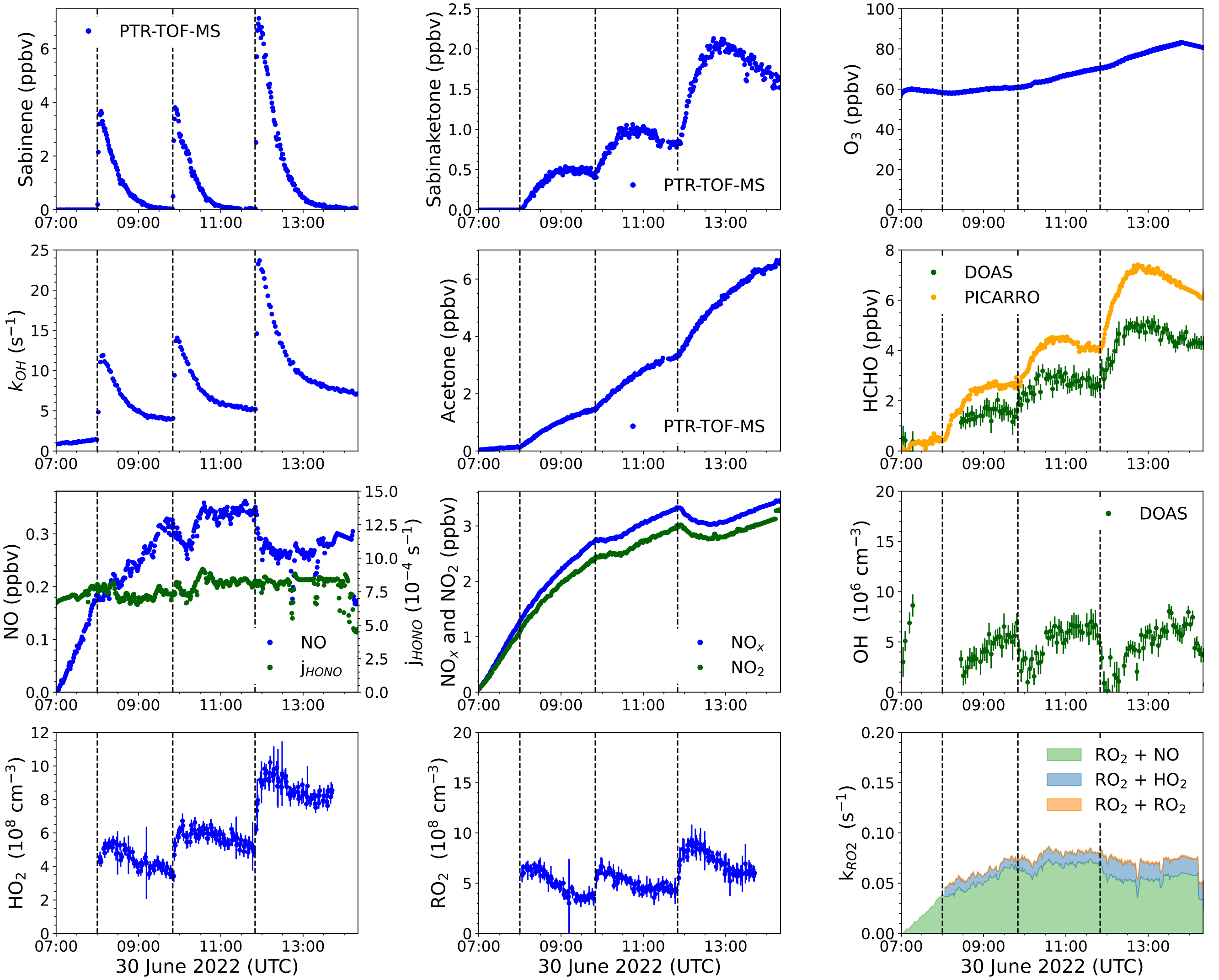

Figure S2. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low NO mixing ratio performed on 30 June 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection.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

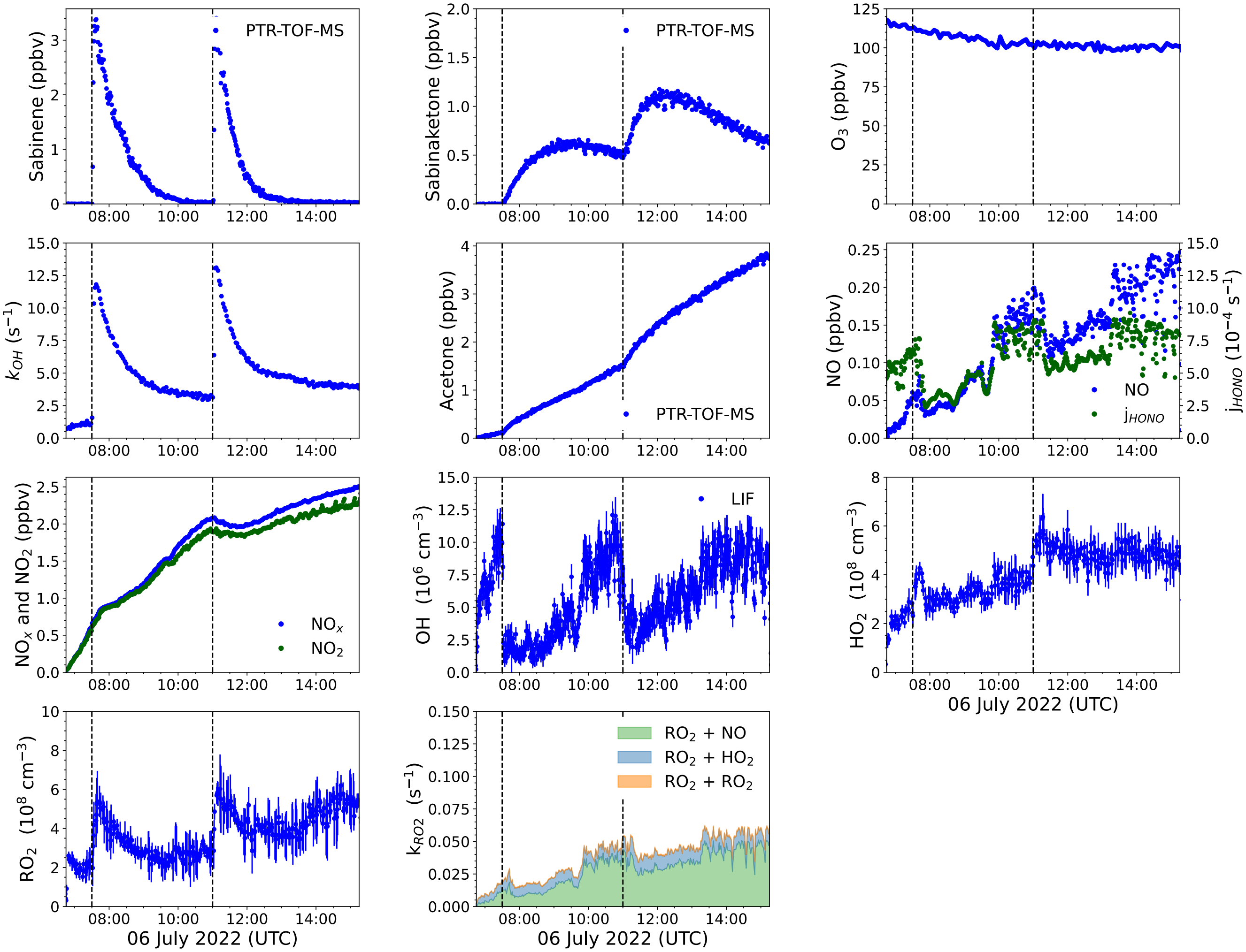

Figure S3. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low NO mixing ratio performed on 06 July 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after the injection.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

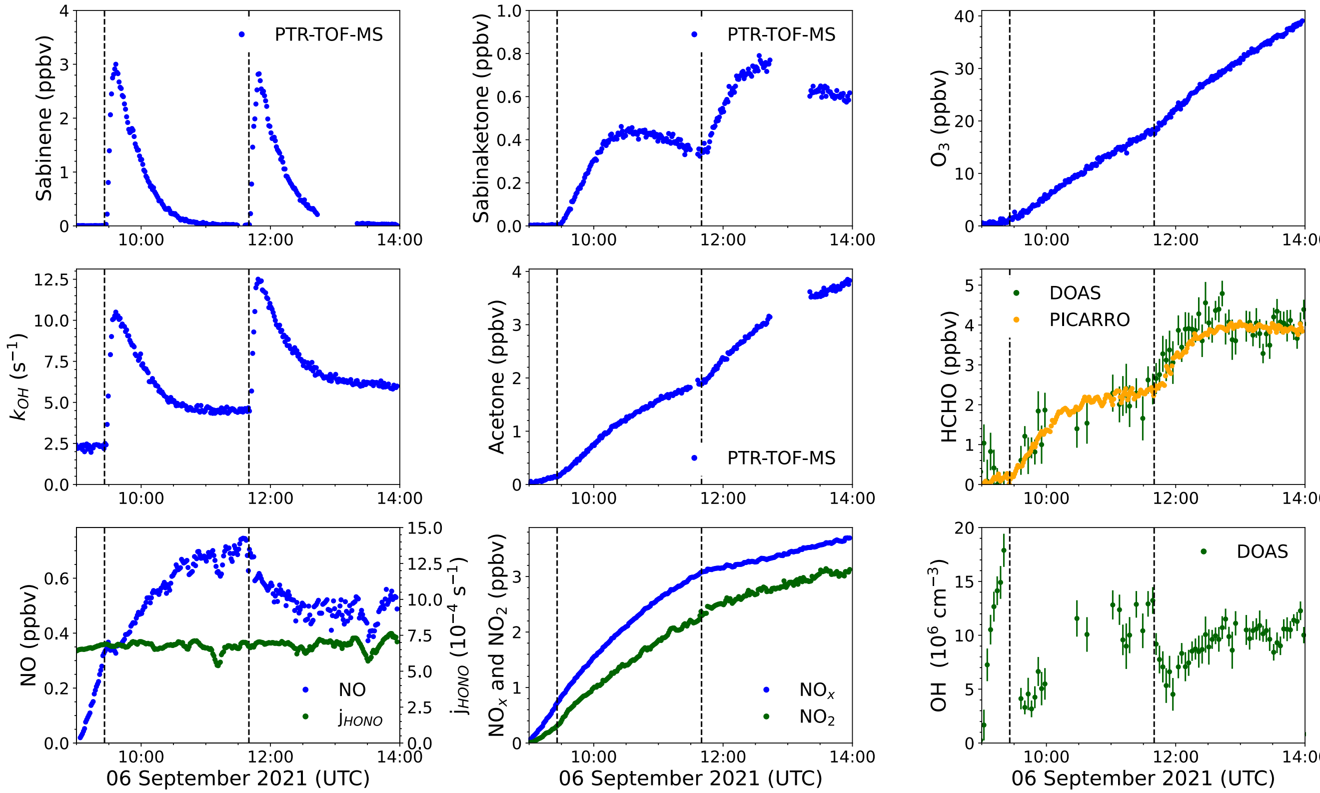

Figure S4. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with medium NO mixing ratio performed on 06 September 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right after 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 avaialble.

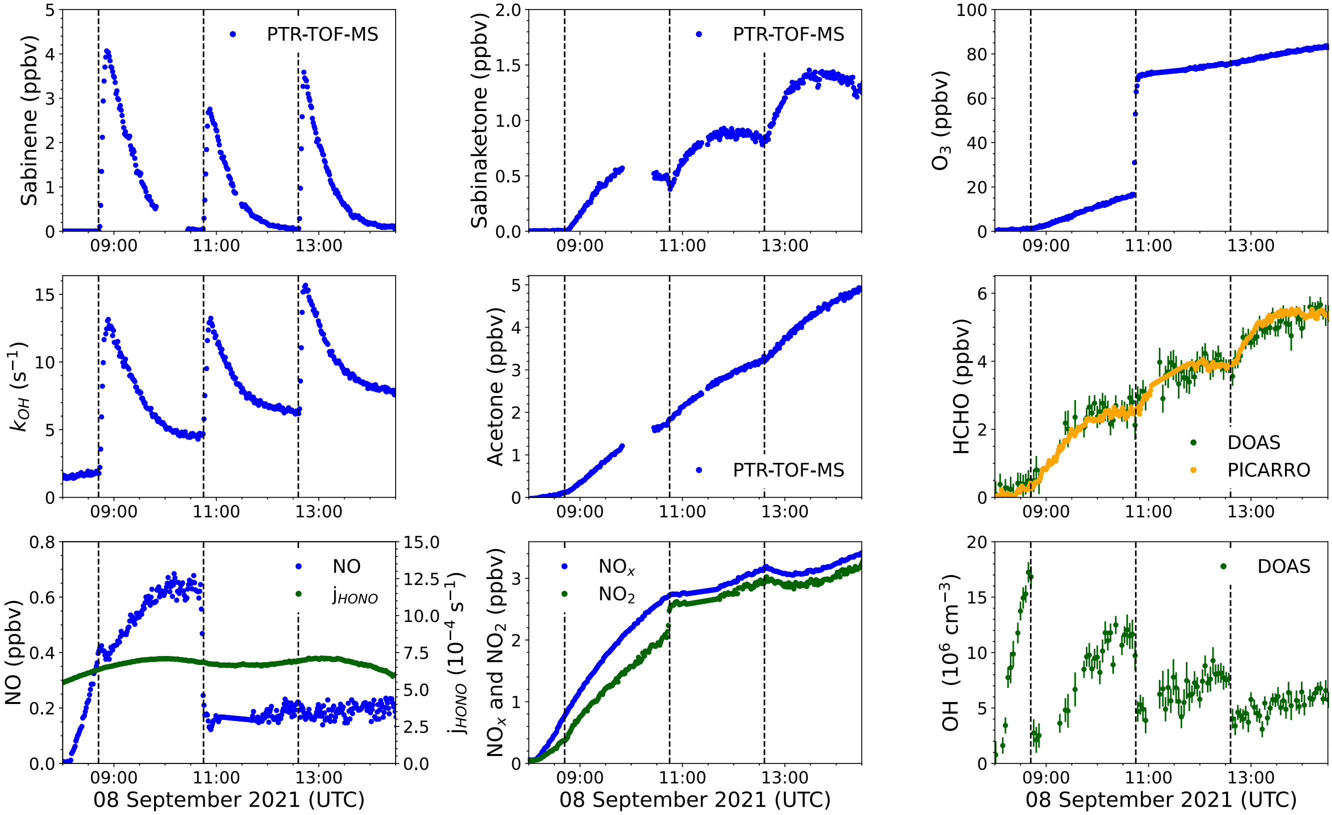

Figure S5. Overview plots of measured radical and trace gas concentrations during the photooxidation experiment with low and medium NO mixing ratio performed on 08 September 2022. PTR-TOF-MS measurements of sabinene were derived from scaling the ion mass signal to the increase of the OH reactivity right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

2. Determination of the reaction rate constant k_{SAB+OH}

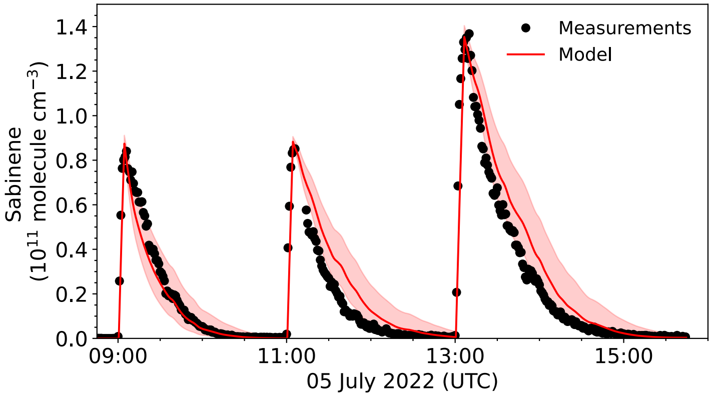

Figure S6. Modelled and measured sabinene concentrations in the photooxidation experiment with medium NO mixing ratios (05 July 2022) used for the determination of the OH reaction rate constant k_{SAB+OH}. The red line and shaded area represent the simulation results applying a value of the OH reaction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

3. Determination of product yields from the oxidation of sabinene

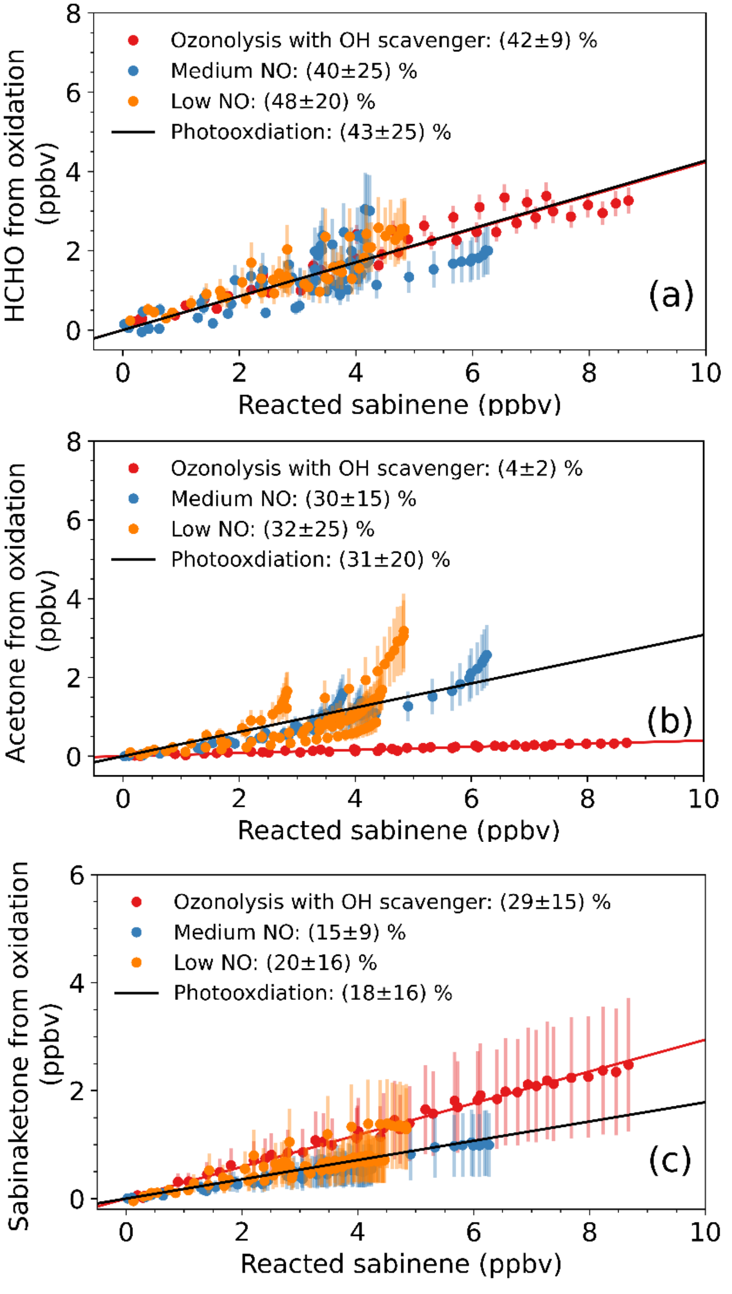

Figure S7. Yields of HCHO (a), acetone (b) and sabinaketone (c) from the photooxidation and ozonolysis of sabinene. The plots are similar to Figure 6 in the main paper, but all data points are included in the regression analysis. Value of the yield named 'Photooxdiation' is the yield calculated from 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, $k_{loss,chem}$, determined in the ozonolysis experiments.

OH scavenger	Experiments	$k_{loss,chem}$ / 10^{-17} cm^3 s^{-1} (without corrections of the reaction HO_2+O_3)	$k_{loss,chem}$ / 10^{-17} cm^3 s^{-1} (with correction of the reaction HO_2 + O_3)
Yes	24 January 2022 2nd injection	4.1±0.4	/
	25 January 2022 3rd injection	3.7±0.4	/
	25 January 2022 4th injection	3.3±0.3	/
	Mean value (i.e., k_{SAB+O3})	3.7±0.5	/
No	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
	$k_{loss,chem}$ (without CO) / $k_{loss,chem}$ (with CO)	1.3±0.2	1.2±0.3
	OH yield	(30±22)%	(18±25)%

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.