



## Supplement of

## Atmospheric photooxidation and ozonolysis of $\Delta^3$ -carene and 3-caronaldehyde: rate constants and product yields

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measured quantity	measurement technique	time	accuracy	LoD
		resolution	$(1\sigma)$	$(1\sigma)$
ОН	laser-induced fluoresence (LIF)	47 s	13 %	$0.7 \times 10^{6}  \mathrm{cm}^{-3}$
$\mathrm{HO}_2,\mathrm{RO}_2$	laser-induced fluoresence (LIF)	$47\mathrm{s}$	16 %	$0.8{\times}10^7{\rm cm}^{-3}$
$k_{ m OH}$	laser photolysis + LIF	$180\mathrm{s}$	10 %	$0.3\mathrm{s}^{-1}$
$\Delta^3$ -carene	proton-transfer-reaction mass-spectrometer	$40\mathrm{s}$	7 %	$2\mathrm{pptv}$
CO	cavity ring-down spectroscopy	$60\mathrm{s}$	1 ppbv	$80\mathrm{ppbv}$
NO	chemiluminescence	$180\mathrm{s}$	5%	$4\mathrm{pptv}$
$NO_2$	chemiluminescence	$180\mathrm{s}$	5%	$2\mathrm{pptv}$
HONO	long-path absorption photometry	300 s	20%	$5\mathrm{pptv}$
$O_3$	UV-absorption	$10\mathrm{s}$	5%	1 ppbv
НСНО	Hantzsch monitor	90 s	8.5 %	$0.1\mathrm{ppbv}$
НСНО	cavity ring-down spectroscopy	$300\mathrm{s}$	$1.5\mathrm{ppbv}$	$0.1\mathrm{ppbv}$
photolysis freq.	spectroradiometer	$60\mathrm{s}$	10 %	a

Table S1 . Instrumentation for radical and trace gas detection in the experiments.

<sup>a</sup> several orders of magnitude lower than the maximum value at noon



Figure S1. Measured and modeled  $\Delta^3$ -carene concentrations for the ozonolysis experiment E4. During the second part of the experiment (upper panel), 90 ppmv of an OH scavenger (CO) were injected to suppress OH, so that  $\Delta^3$ -carene reacted only with ozone. The modeled decay is fitted with a rate constant of  $(4.4 \pm 0.2) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ . During the first part of the experiment (lower panel), when no CO was present, the measured decay of  $\Delta^3$ -carene is significantly faster than expected from ozonolysis alone. The measured time series of  $\Delta^3$ -carene can be best matched, if an OH yield of  $0.65 \pm 0.10$  from its ozonolysis reaction is assumed. OH yields of 0.20, 0.40 and 0.80 are also presented in the lower panel to demonstrate the sensitivity of the system to changes in the OH yield.



Figure S2. Overview of measured concentrations for selected species in the SAPHIR chamber for the  $\Delta^3$ -carene + OH oxidation experiment with low NOx conditions on E2. Dashed lines indicate times when  $\Delta^3$ -carene was injected into the chamber.



Figure S3. Overview of measured concentrations for selected species in the SAPHIR chamber for the caronaldehyde photooxidation experiments E5. The shaded area indicates the time where CO was injected as an OH scaveger (experiment E6). Dashed lines indicate times when caronaldehyde was injected into the chamber.



Figure S4. Timeseries of Q(HONO),  $k_{OH+NO} \times OH \times NO$  and  $j_{HONO} \times HONO$  used to calculate the organic nitrate yield of the OH +  $\Delta^3$ -carene in the main text (see Section 2.5).