Investigation of the α-pinene photooxidation by OH in the atmospheric simulation chamber SAPHIR

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Supplement

S1 Calculation of product yields

To calculate the yield as described in Galloway et al. (2011) and Kaminski et al. (2017) it is necessary to correct measured concentrations for losses and additional sources. The correction term for the example of pinonaldehyde is shown in Eq. S1:

$$c_{\text{pinal corr}}[i] = c_{\text{pinal}}[i-1] + \Delta c_{\text{pinal}} + \Delta c_{\text{dil}} + \Delta c_{\text{rl}} + \Delta c_{\text{pl}} - \Delta c_{\text{O3}} \tag{S1}$$

To obtain the corrected pinonaldehyde concentration $c_{\text{pinal corr}}$ the measured concentration c_{pinal} has to be corrected for losses by photolysis Δc_{pl}, dilution Δc_{dil} and the reaction with OH radicals Δc_{rl}, as well as a source from the ozonolysis of α-pinene Δc_{O3}. The different terms are further explained in the equations S2 to S5:

$$\Delta c_{\text{dil}} = c_{\text{pinal}}[i-1] * \Delta t * k_{\text{dil}}[i-1] \tag{S2}$$

$$\Delta c_{\text{rl}} = c_{\text{pinal}}[i-1] * \Delta t * c_{\text{OH}}[i-1] * k_{\text{pinal + OH}} \tag{S3}$$

$$\Delta c_{\text{pl}} = c_{\text{pinal}}[i-1] * \Delta t * J_{\text{pinal}}[i-1] \tag{S4}$$

$$\Delta c_{\text{O3}} = c_{\text{pinal}}[i-1] * \Delta t * c_{\text{O3}}[i-1] * k_{\text{apinene + O3}} \tag{S5}$$

$c_{\text{pinal corr}}[i]$: corrected pinonaldehyde concentration at time i

$c_{\text{pinal}}[i-1]$: measured pinonaldehyde concentration at time i-1

Δc_{dil} : dilution

Δc_{rl} : loss due to the reaction with OH

5   Δc_{pl} : photolytic loss

Δc_{O3} : production from ozonolysis

$c_{\text{OH}}[i-1]$: measured OH concentration by DOAS at time i-1

$k_{\text{pinal + OH}}$: reaction rate of pinonaldehyde + OH (Atkinson et al., 2006)

$J_{\text{pinal}}[i-1]$: measured photolysis frequency at time i-1

10    $c_{\text{O3}}[i-1]$: O_3 concentration at time i-1

$k_{\text{apinene + O3}}$: reaction rate of α-pinene + O_3 (MCM, 2019)

An overview of all corrections made for the different species is shown in Table S1.

species	corrected for	
	losses by	sources from
α-pinene	α-pinene + O_3 dilution	/
pinonaldehyde	pinonaldehyde + hν pinonaldehyde + OH dilution	α-pinene + O_3
acetone	acetone + OH dilution	chamber wall
HCHO	HCHO + OH HCHO + hν dilution	CH$_3$CHO + OH chamber wall

Table S1. Overview of correction terms for the analysed species applied in the yield calculation.

Fig. S1 shows the measured (blue) and corrected concentrations (red). For α-pinene the amount of reacted substance is accumulated over the whole duration of the experiment and corrected for losses by ozonolysis and dilution. The corrected

15   HCHO, acetone and pinonaldehyde are then plotted versus the corrected amount of reacted α-pinene. The yield of the reaction α-pinene + OH is derived from the resulting slopes.
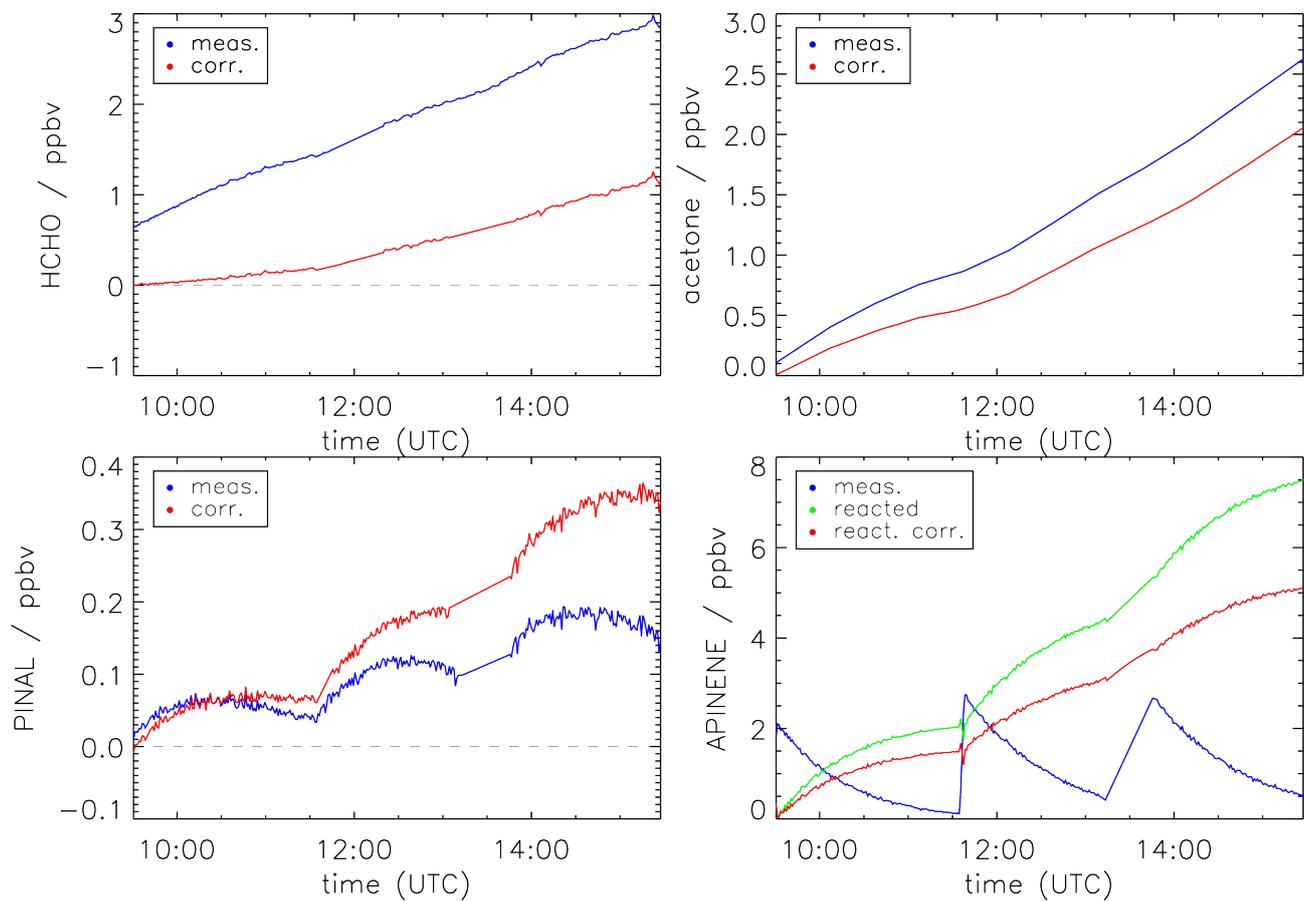
Figure S1. The blue curves show the measured concentrations. For α-pinene the green curve represents the amount of reacted substance. The individual concentrations after the applied correction are shown in red.

S2 Model modifications for M1 sensitivity study

All additions made in the sensitivity run M1 based on the suggestions by Vereecken et al. (2007) are shown in Tables S2 and S3. The naming schema of reactants starting with an "R" is according to Vereecken et al. (2007). Table S2 shows the initial oxidation step of the OH attack, and the subsequent chemistry of the RO_2 after the OH addition.

5   For simplification only one out of three hydrogen-abstraction pathways is included here forming compound ROOA. The subsequent chemistry of ROOA is shown in Table S3.

APINCO2 was replaced by synR1 and antiR1 as the mechanism by Vereecken et al. (2007) distinguishes the syn and anti stereoisomers of this compound following different pathways. Both synR1 and antiR1 can react with NO but this pathway is outrun by the unimolecular reactions 1,6-H shift, which is only happening for anti isomer, and the ring-closure forming R4.

10   The late degradation products after the 1,6-H-shift are 8-OOH-menthen-6-one (R7P1) and 2-OH-OOH-menthen-6-one (R9P1). The ring-closure leads to the formation of a dicarbonyl cycloperoxide (R5P1).

The model introduced new RO_2, which are not been part of the MCM, and a substantial fraction of the total reaction procedes through these pathways. This underestimates the HO_2 loss by the reaction of RO_2 + OH, especially in the sensitivity run M2. Therefore the RO_2 + HO_2 reactions in the lower half of Table S3 are added.

Table S2. Additional and modified reactions applied to the MCM based on the proposed mechanism by Vereecken et al. (2007). For additional OH abstraction chemistry see Table S3. All nitrate species are lumped as one species RNO3.

reaction	reaction rate constant
APINENE + OH→ROOA	$0.12 \times 1.2 \times 10^{-11} \exp(440K/T) \, cm^3 s^{-1}$
APINENE + OH→APINAO2	$0.22 \times 1.2 \times 10^{-11} \exp(440K/T) \, cm^3 s^{-1}$
APINENE + OH→APINBO2	$0.44 \times 1.2 \times 10^{-11} \exp(440K/T) \, cm^3 s^{-1}$
APINENE + OH→synR1	$0.4 \times 0.22 \times 1.2 \times 10^{-11} \exp(440K/T) \, cm^3 s^{-1}$
APINENE + OH→antiR1	$0.6 \times 0.22 \times 1.2 \times 10^{-11} \exp(440K/T) \, cm^3 s^{-1}$
APINAO2 + NO→APINANO3	$0.03 \times$ KRO2NO[a]
APINAO2 + NO→APINAO + NO2	$0.97 \times$ KRO2NO[a]
APINAO →PINAL + HO2	$0.875 \times$ KDEC[b]
APINAO →HCHO + HO2	$0.125 \times$ KDEC[b]
APINBO2 + NO→APINBNO3	$0.07 \times$ KRO2NO[a]
APINBO2 + NO→APINBO + NO2	$0.93 \times$ KRO2NO[a]
antiR1 + NO →R2 + NO2	KRO2NO[a]
antiR1 →R4	$0.6 \, s^{-1}$
antiR1 →R7	$11.5 \, s^{-1}$
synR1 + NO→R2 + NO2	KRO2NO[a]
synR1 →R4	$2.6 \, s^{-1}$
R2 →R2P1 + CH3COCH3 + HO2	KDEC[b]
R4 + NO→RNO3	$0.1 \times$ KRO2NO[a]
R4 + NO→R5 + NO2	$0.9 \times$ KRO2NO[a]
R5 →R5P1 + HO2	KDEC[b]
R7 →R8	$0.5 \times$ KDEC[b]
R7 →R7P1 + HO2	$0.5 \times$ KDEC[b]
R8 + NO→RNO3	$0.29 \times$ KRO2NO[a]
R8 + NO→R9 + NO2	$0.71 \times$ KRO2NO[a]
R9 →R9P1 + HO2	KDEC[b]

[a] value from MCM: KRO2NO= $2.7 \times 10^{-12} \exp(360K/T) \, cm^3 s^{-1}$ (MCM, 2019)
[b] value from MCM: KDEC= 1.0×10^6 (MCM, 2019)

Table S3. Additional OH abstraction reactions and subsequent product reactions applied to the MCM based on the proposed mechanism by Vereecken et al. (2007). All nitrate species are lumped as one species RNO3. All reaction products of $RO_2 + HO_2$ are lumped as one species RRO2.

reaction	reaction rate constant
ROOA + NO→RNO3	$0.11\times$ KRO2NO[a]
ROOA + NO→ROA + NO2	$0.89\times$ KRO2NO[a]
ROA →ROOB	$0.6\times$ KDEC[b]
ROA →ROOC	$0.4\times$ KDEC[b]
ROOB + NO→RNO3	$0.11\times$ KRO2NO[a]
ROOB + NO→ROB + NO2	$0.89\times$ KRO2NO[a]
ROB →CH3COCH3+HCHO + HO2	KDEC[b]
ROOC + NO→RNO3	$0.11\times$ KRO2NO[a]
ROOC + NO→ROC + NO2	$0.89\times$ KRO2NO[a]
ROC →HCHO+HO2	KDEC[b]
synR1 + HO2→ APINCOOH	KRO2HO2[c]
antiR1 + HO2→ APINCOOH	KRO2HO2[c]
R4 + HO2→ RRO2	KRO2HO2[c]
R8 + HO2→ RRO2	KRO2HO2[c]
R10 + HO2→ RRO2	KRO2HO2[c]
R12 + HO2→ RRO2	KRO2HO2[c]
ROOA + HO2→ RRO2	KRO2HO2[c]
ROOB + HO2→ RRO2	KRO2HO2[c]
ROOC + HO2→ RRO2	KRO2HO2[c]

[a] value from MCM: KRO2NO$= 2.7 \times 10^{-12} \exp(360K/T)\, cm^3 s^{-1}$ (MCM, 2019)

[b] value from MCM: KDEC$= 1.0 \times 10^6$ (MCM, 2019)

[c] value from MCM: KRO2HO2$= 2.9110^{-13} \exp(1300K/T)\, cm^3 s^{-1}$ (MCM, 2019)

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