Supplement "Development of a chemical mechanism to improve secondary organic aerosol formation in the box model CAABAMECCA (version 4.5.6-rc.1)"

Reaction kinetics and mechanisms

Table S1. Summary of rate constants and substituent factors used in the new mechanism. (adapted from Taraborrelli (2010))

Variable	**Rate constant / substituent factor**	**Description / substituent**
H-abstraction by OH		
k_p	$4.49 \cdot 10^{-18} \cdot T^2 \cdot \exp(-320/T)$	Primary H-abstraction
k_s	$4.50 \cdot 10^{-18} \cdot T^2 \cdot \exp(253/T)$	Secondary H-abstraction
k_t	$2.12 \cdot 10^{-18} \cdot T^2 \cdot \exp(696/T)$	Tertiary H-abstraction
Substituent factor f		
f_{sOH}	3.44	OH at sec. carbon
f_{tOH}	2.68	OH at tert. carbon
f_{sOOH}	8.00	OOH at tert. carbon
f_{tOOH}	8.00	OOH at sec. carbon
f_{CHO}	0.55	aldehyde
f_{CO2H}	1.67	carbonic acid
f_{O}	8.15	double bond to O
OH-addition to double bonds		
k_{adp}	$4.5 \cdot 10^{-12} \cdot (T/300)^{-0.85}$	primary carbon of double bond
k_{ads}	$0.25 \cdot (1.1 \cdot 10^{-11} \cdot \exp(485/T)$ $+1.0 \cdot 10^{-11} \cdot \exp(553/T))$	secondary carbon of double bond
k_{adt}	$1.92 \cdot 10^{-11} \cdot \exp(450/T) - k_{ads}$	tertiary carbon of double bond
Substituent factor a		
a_{CHO}	0.31	aldehyde
a_{COCH3}	0.76	ketone
a_{CH2OH}	1.7	alcohol
a_{CH2OOH}	1.7	hydroperoxide
NO reaction with peroxidy radicals		
K_{RO2NO}	$2.54 \cdot 10^{-12} \cdot \exp(360/T)$	all branches (NO-add. & O-abst.)
HO_2 reaction with peroxy radicals		
k_{RO2HO2}	$2.91 \cdot 10^{-13} \cdot \exp(1300/T) \cdot$ $(1 - \exp(-0.245 \cdot n_C))$	all branches (H-add. & O-abst.) n_C = number of carbon
HO_2 reaction with peroxy radicals		
k_{RO2NO3}	$2.30 \cdot 10^{-12}$	O-abstraction
H abstraction to OOH by OH		
k_{ROOHRO}	$0.6 \cdot (5.3 \cdot 10^{-12} \cdot \exp(190/T))$	H-abstraction only OOH

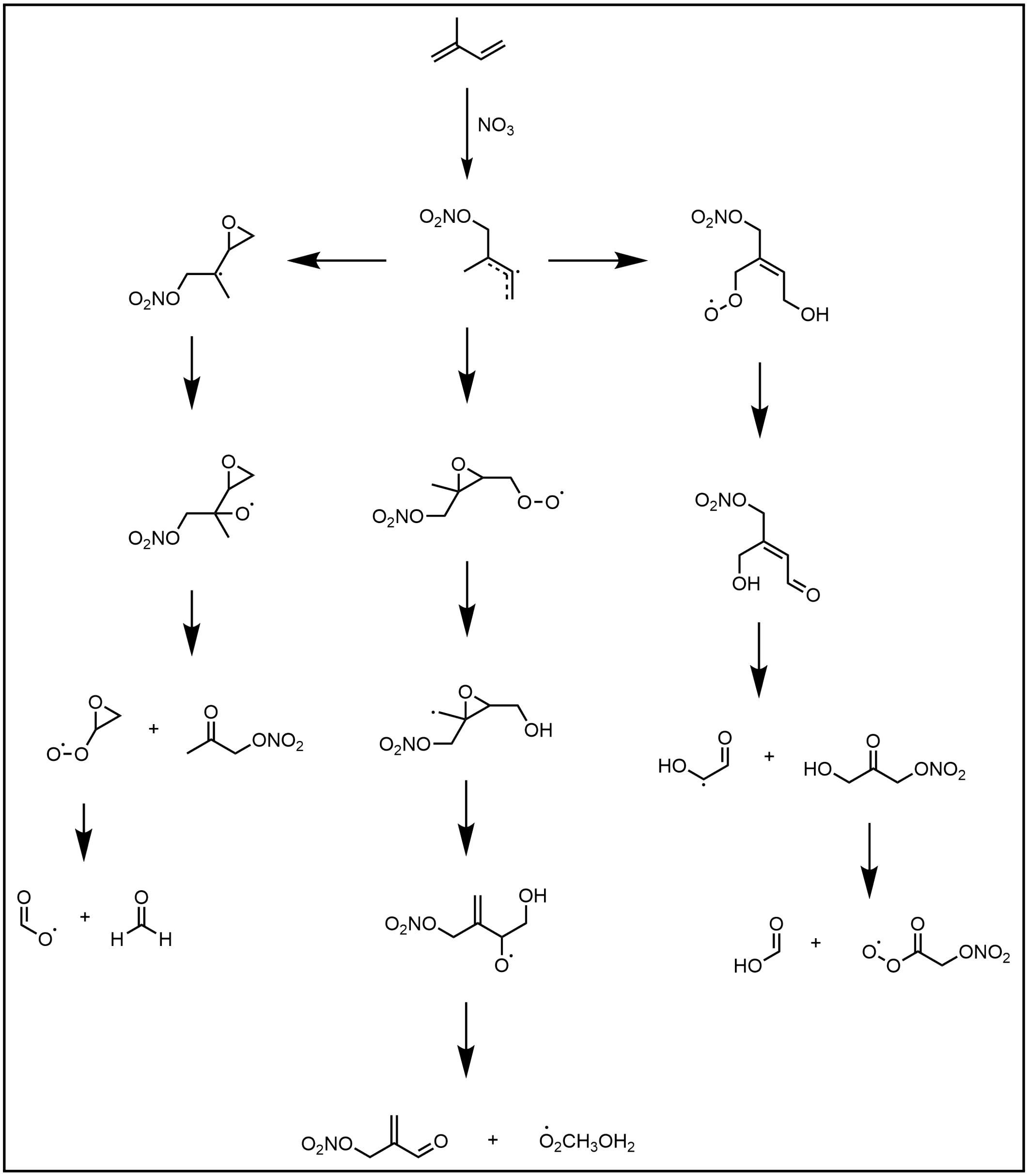

Figure S1. Simplified scheme of the updated isoprene + NO_3 mechanism. Only the mechanism for the trans-isomer, formed by the addition of NO_3, is shown. This accounts for 50% of the products. The cis-isomer is implemented as well and yields similar products.

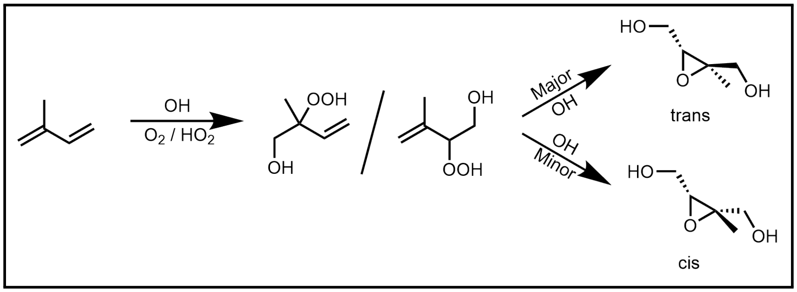

Figure S2. Isoprene oxidation pathway resulting in the formation of trans- and cis-IEPOX. Only the major Isomers of ISOPOOH (center) are shown, but all isomers as well as the corresponding products are implemented into MECCA. In chamber experiments 33% trans- and 67% cis-IEPOX (1,2-ISOPOOH) is produced, while the formation ratio is depending on the observed ISOPOOH isomere (St. Clair et al., 2016; Bates et al., 2014).

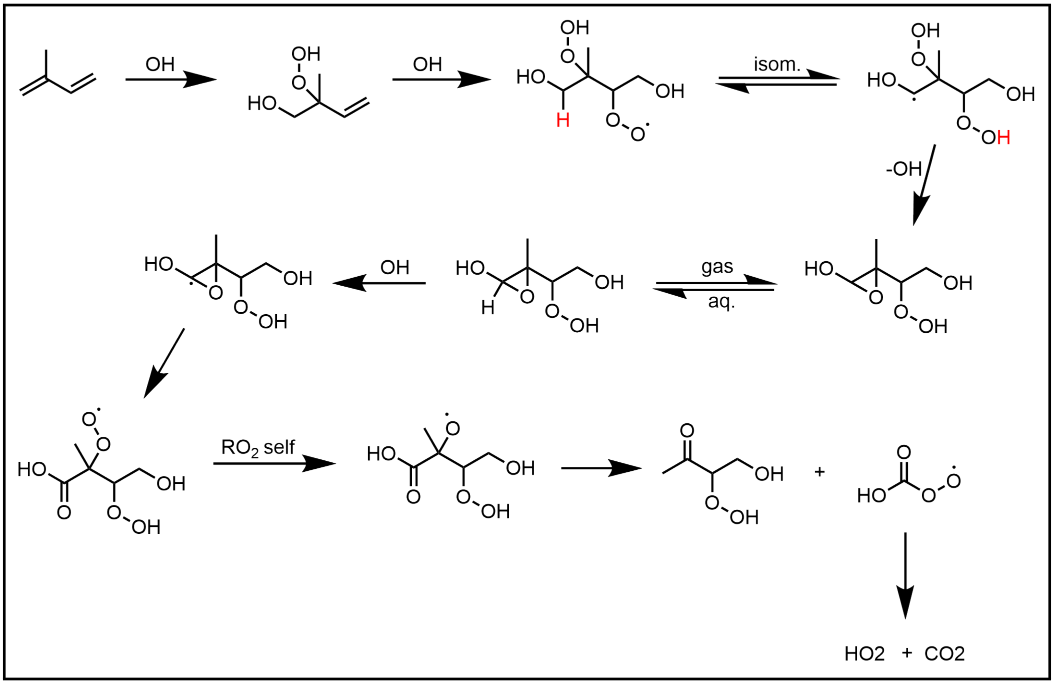

Figure S3. Isoprene OH oxidation refering to results by D'Ambro et al. (2017) and further aqueous degradation.

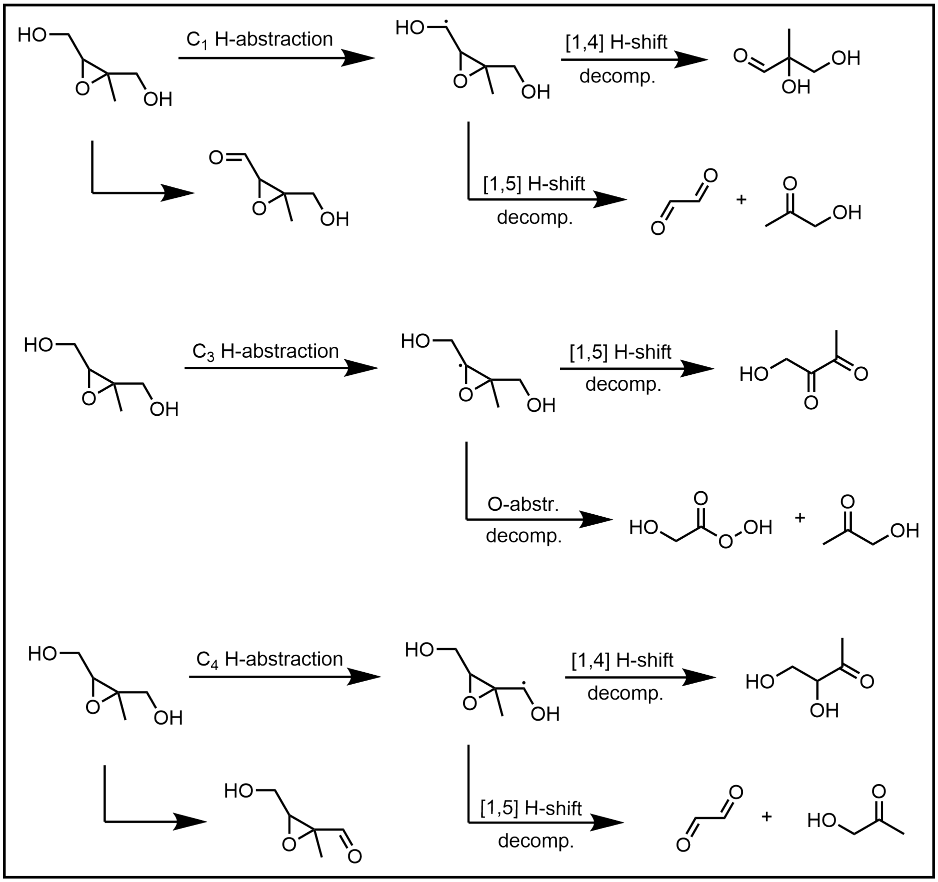

Figure S4. Simplified mechanism of the IEPOX gas-phase oxidation. H-abstraction is shown for the three main abstraction sites at C1, C3 and C4. Formed alkyl nitrates and hydroperoxides are not displayed. The aldehyde directly formed from IEPOX (IEPOXO) is lumped into one species. The degradation of the lumped IEPOXO is considered. A similar mechanism is implemented for delta-IEPOX.

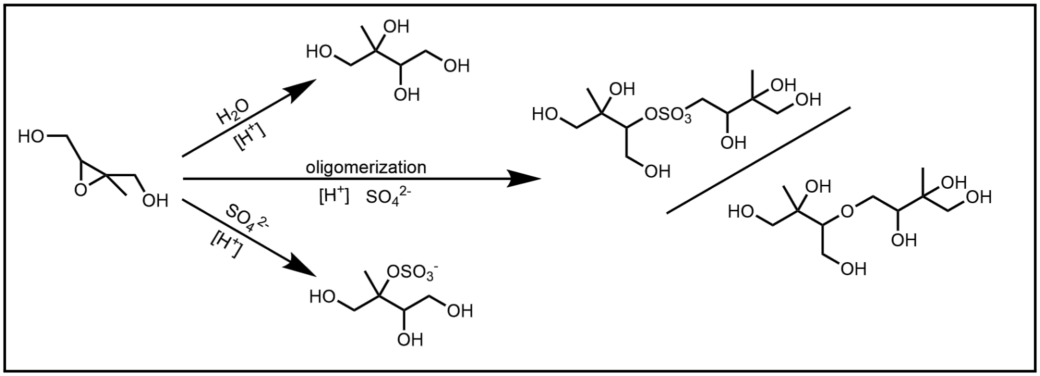

Figure S5. Acid catalyzed Ring opening mechanism of IEPOX in the aqueous phase. Water and sulfate are considered possible nucleophiles, leading to tetrols and organosulfates. Other nucleophiles exhibit slower kinetics. At high IEPOX and tetrol/organosulfate concentration, oligomerization reaction are also accessible.

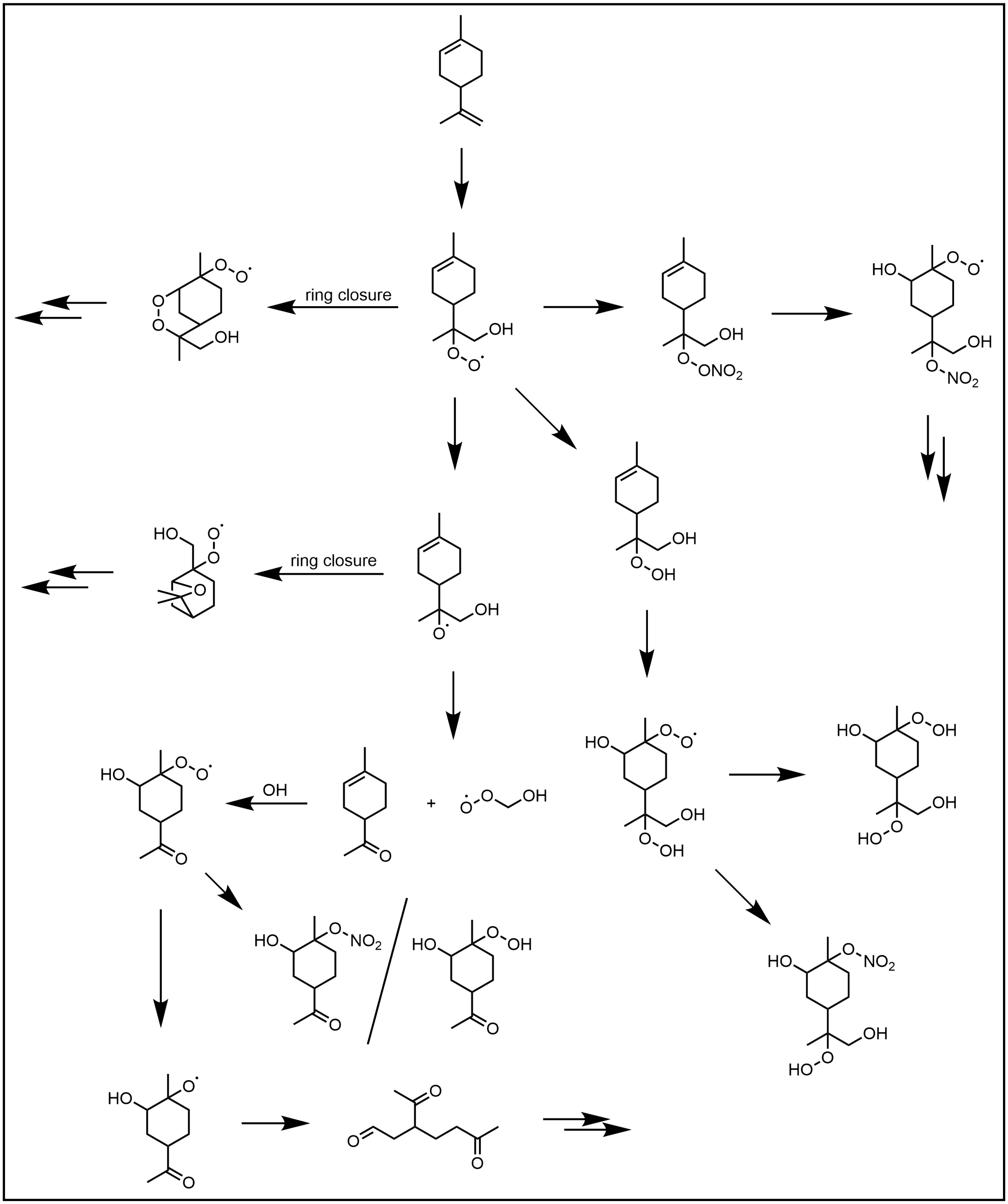

Figure S6. Exemplary cutout of the limonene OH oxidation reaction mechanism. Addition of an hydroxyl radical to the external double bond.

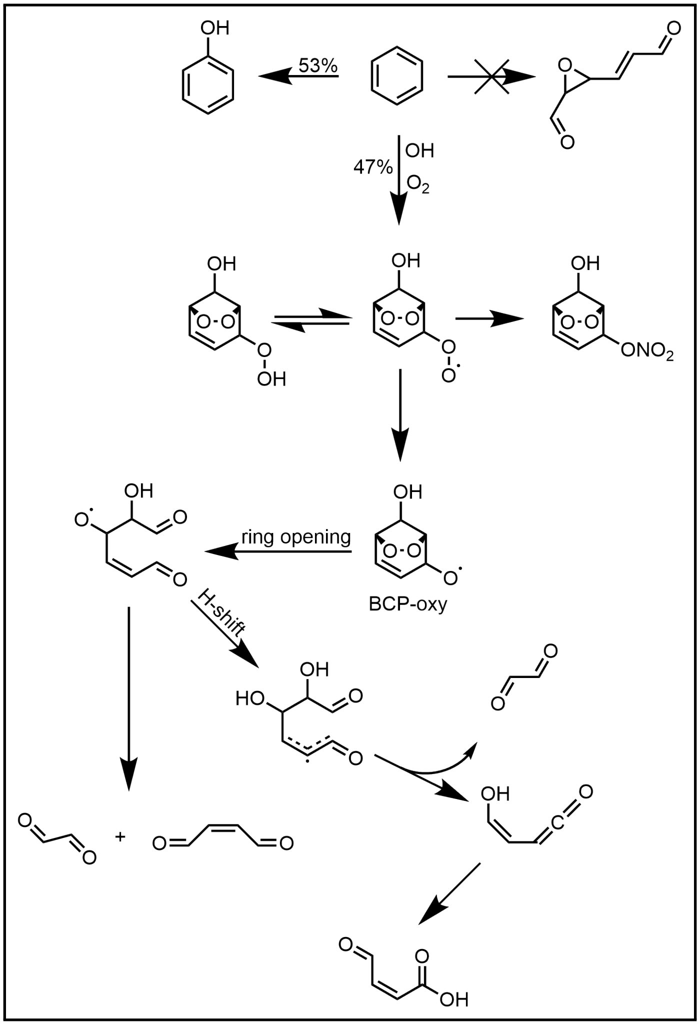

Figure S7. Mechanism for the oxidation of benzene by OH. The initial reaction yielding epoxides is excluded, as it was found to have a very low yield (Xu et al., 2020). The yield was redistributed to the BCP-oxy pathway. Additionally, the BCP-oxy pathway was refined by implementing a new ring-opening reaction and the degradation of the formed product.

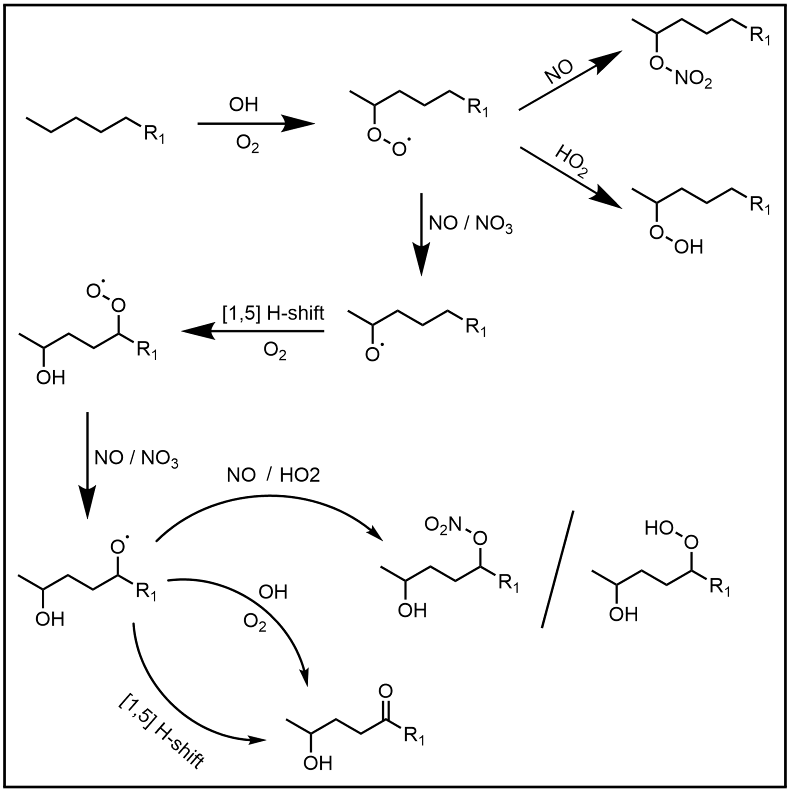

Figure S8. Mechanism of the hexane oxidation yielding hydroperoxides, alkyl nitrates and oxidized hexanes. A similar mechanism is implemented for pentane, heptane and octane.

Henry's law solubility constants

Table S2. Newly implemented Henry's law solubility constants H_s estimated by GROHME, and the temperature-dependence factor $B = \mathrm{d}\ln H_\mathrm{s}/\mathrm{d}(1/T)$ calculated with the method of Kühne et al. (2005).

compound	**SMILES**	H_s **/ M/atm**	$\mathrm{d}\ln H_\mathrm{s}/\mathrm{d}(1/T)$ **/ K**
IEPOX + OH			
LIEPOXO	CC1(CO)OC1C=O	2.1E6	13700
LDIEPOXO	CC1(C(=O)CO)CO1	1.3E5	13700
LIEPOXCO3H	CC1(C(=O)OO)OC1O	9.1E4	14400
LTRIOL	C(O)C(O)C=C(C)(O)	4.9E9	11100
METHFDIOL	C1C(O)-O-C(O)C1(C)	9.1E7	10900
METETROL	C(O)C(O)C(C)(O)C(O)	6.2E12	13600
METRICO	C(O)C(C)(O)C(=O)C(O)	7.4E8	11500
MEDICO4CO	C(=O)C(C)(O)C(=O)C(O)	3.1E8	12100
MEDICO1CO	C(=O)C(=O)C(O)(C)C(O)	2.5E9	12100
Isoprene + $\mathrm{NO_3}$			
ISOP1N4OOH (E/Z)	C/C(=C\COO)CON(=O)=O	9.8E4	11400
ISOP1N4ONO2 (E/Z)	C/C(=C\CON(=O)=O)CON(=O)=O	2.6E2	9400
LHC4ACCHO	C/C(C=O)=C/CO	1.2E5	10600
EPXISOPNONO2	CC(CON(=O)=O)(ON(=O)=O)C1CO1	5.4E3	12500
ISOP1N5ONO2	O=N(=O)OC/C(=C\CO)CON(=O)=O	5.9E6	13300
ISOP1N5OOH	O=N(=O)OC/C(=C/CO)COO	2.3E9	14300
ISOP1N6CO	O=C/C(=C\CO)CON(=O)=O	2.1E7	14000
ISOP1N2ONO2	C=CC(C)(CON(=O)=O)ON(=O)=O	1.6E2	9400
LISOP1N23O4CO	CC1(CON(=O)=O)OC1C=O	1.5E5	12400
LISOP1N23O4ONO2	CC1(CON(=O)=O)OC1CON(=O)=O	4.6E3	12500
Large Alkanes + OH			
C5H112ONO2	CC(ON(=O)(=O))CCC	3.4E-1	6000
C5H112O2H	CC(OO)CCCCC(OO)CCC	1.4E2	7000
C5OHONO2	C(ON(=O)(=O))CCC(O)C	2.1E3	9900
C5OHOOH	C(OO)CCC(O)C	7.2E5	10900
C5OHCO	C(O)CCC(=O)C	3.6E5	9800
C6H13ONO2	CC(ON(=O)(=O))CCCC	3.1E-2	6300
C6H13O2H	CC(OO)CCCC	1.0E2	7300
C6OHONO2	CC(ON(=O)(=O))CCC(O)C	1.6E3	10200
C6OHOOH	CC(OO)CCC(O)C	5.5E5	11200
C6OHCO	CC(O)CCC(=O)C	2.8E5	10100

Table S2. Newly implemented Henry's law constants estimated by GROHME, and the temperature-dependence factor $B = \mathrm{d}\ln H_\mathrm{s}/\mathrm{d}(1/T)$ calculated with the method of Kühne et al. (2005). (continued)

compound	**SMILES**	H_s **/ M/atm**	$\mathrm{d}\ln H_\mathrm{s}/\mathrm{d}(1/T)$ **/ K**
Large Alkanes + OH			
C7H15ONO2	CC(ON(=O)(=O))CCCCC	2.3E-1	6600
C7H15O2H	CC(OO)CCCCC	7.8E1	7600
C7OHONO2	CCC(ON(=O)(=O))CCC(O)C	1.2E3	10600
C7OHOOH	CCC(OO)CCC(O)C	4.2E5	11600
LC7OHCO	CCC(O)CCC(=O)C	2.1E5	10500
C8H17ONO2	CC(ON(=O)(=O))CCCCCC	6.9E2	7000
C8H17O2H	CC(OO)CCCCCC	5.9E1	8000
C8OHONO2	CCCC(ON(=O)(=O))CCC(O)C	9.1E2	10900
C8OHOOH	CCCC(OO)CCC(O)C	3.2E5	11900
LC8OHCO	CCCC(O)CCC(=O)C	1.6E5	10800
Limonene			
HOC2H4CHO	O=CCCO	3.6E3	9900
C517OOH	CC(=O)C(CO)COO	1.1E8	13400
HMVKBCHO	CC(=O)C(C=O)CO	3.6E7	10800
CO2C4CHO	CC(=O)CCC=O	5.6E4	8400
C519OOH	CC(=O)C(CCO)OO	1.7E7	13400
C517CHO	CC(=O)C(CO)CC=O	9.6E4	12700
C622OOH	C=C(C)C(CO)COO	1.3E6	12000
C519CHO	CC(=O)C(C=O)CCO	2.8E8	11100
C622ONO2	C=C(C)C(CO)CON(=O)=O	3.5E3	11000
C622CHO	C=C(C)C(CO)CC=O	5.9E5	11300
C728OOH	CC(CO)(OO)C(CO)CC=O	5.4E12	18100
C727OOH	CC(=O)CCC(OO)C(C)=O	2.0E7	12700
C624CHO	C=C(C)C(C=O)CCO	5.9E5	11300
C730OOH	CC(CO)(OO)C(C=O)CCO	6.2E12	18100
C728ONO2	CC(CO)(ON(=O)=O)C(CO)CC=O	1.5E10	17100
C622CONO2	C=C(C)C(CO)CC(=O)ON(=O)=O	1.0E5	13900
C730ONO2	CC(CO)(ON(=O)=O)C(C=O)CCO	3.5E11	17100
C818CO	CC(=O)C(=O)CC(CO)C(C)=O	6.6E8	15900
C816CO	C=C(C)C(=O)CCC(C)=O	3.1E4	10200
C819OOH	CC(=O)CCC(=O)C(C)(CO)OO	2.1E9	17000
C817CO	CC(=O)CCC(C=O)C(C)=O	3.1E7	12000
C817OOH	CC(=O)CCC(COO)C(C)=O	1.2E8	13000
C818OOH	CC(=O)C(CO)CC(OO)C(C)=O	5.8E10	17000
C729CHO	C=C(C)C(CC=O)CC=O	8.1E4	10200
C822OOH	C=C(C)C(CC=O)CCOO	8.9E5	11300

Table S2. Newly implemented Henry's law constants estimated by GROHME, and the temperature-dependence factor $B = \mathrm{d}\ln H_\mathrm{s}/\mathrm{d}(1/T)$ calculated with the method of Kühne et al. (2005). (continued)

compound	**SMILES**	H_s **/ M/atm**	$\mathrm{d}\ln H_\mathrm{s}/\mathrm{d}(1/T)$ **/ K**
Limonene			
C824OOH	C=C(C)C(CCO)C(C=O)OO	8.5E8	15300
RO5R5	CC(C)(OC=O)C(CO)CC=O	1.3E7	17300
C819ONO2	CC(=O)CCC(=O)C(C)(CO)ON(=O)=O	4.0E8	16000
C817ONO2	CC(=O)CCC(CON(=O)=O)C(C)=O	4.0E6	12000
C822ONO2	C=C(C)C(CC=O)CCON(=O)=O	2.9E3	10300
C824ONO2	C=C(C)C(CCO)C(C=O)ON(=O)=O	9.6E8	14300
C923OOH	C=C(C)C(CCC(C)=O)COO	1.1E6	11700
C923OH	C=C(C)C(CO)CCC(C)=O	5.4E5	12000
NORLIMAL	C=C(C)C(C=O)CCC(C)=O	6.2E4	10600
C924OOH	C=C(C)C(CO)CC(OO)C(C)=O	3.0E8	15600
C924OH	C=C(C)C(CO)CC(O)C(C)=O	3.8E7	15900
LMLKET	CC(=O)CCC(CC=O)C(C)=O	1.1E8	13000
LIMKET	CC1=CCC(C(C)=O)CC1	6.5E1	8000
C817CO3H	CC(=O)CCC(CC(=O)OO)C(C)=O	3.4E9	15900
C822CO3H	C=C(C)C(CC=O)CCC(=O)OO	1.7E6	14200
C822CO2H	C=C(C)C(CC=O)CCC(=O)O	4.5E6	14500
C91ONO2	C=C(C)C(CCC(C)=O)CON(=O)=O	3.2E3	10700
NORLIMONO2	CC(=O)CCC(C=O)C(C)(CO)ON(=O)=O	3.8E10	16300
C92ONO2	C=C(C)C(CO)CC(ON(=O)=O)C(C)=O	4.8E7	14600
C817CONO2	CC(=O)CCC(CC(=O)ON(=O)=O)C(C)=O	1.2E7	14900
C822CONO2	C=C(C)C(CC=O)CCC(=O)ON(=O)=O	6.3E3	13200
LABPINCOOH	CC1=CCC(C(C)(CO)OO)CC1	3.6E6	13400
RO5R1O2H	CC1(C)OC2CC1CCC2(CO)OO	1.0E8	16600
RO5R2O2H	CC1(C)OC(OO)CC1CCC(=O)CO	1.8E9	19100
RO5R3O2H	CC(C)(OC=O)C(CCC(=O)CO)COO	7.8E9	21600
RO5R4O2H	CC(C)(OC=O)C(CO)CC(OO)C(=O)CO	3.6E12	24000
C923CO3H	C=C(C)C(CCC(C)=O)CC(=O)OO	2.2E6	14500
LIMONONIC	C=C(C)C(CCC(C)=O)CC(=O)O	5.8E6	14900
LIMAL	C=C(C)C(CC=O)CCC(C)=O	4.1E4	10900
LIMALOOH	CC(=O)CCC(CC=O)C(C)(CO)OO	4.4E12	17700
LIMALOH	CC(=O)CCC(CC=O)C(C)(O)CO	2.2E12	18000
LIMALAOOH	C=C(C)C(CC=O)CC(OO)C(C)=O	2.5E7	14500
LIMALAOH	C=C(C)C(CC=O)CC(O)C(C)=O	3.1E6	14900
LIMALACO	C=C(C)C(CC=O)CC(=O)C(C)=O	4.4E6	13400
LIMALBOOH	C=C(C)C(CC=O)CCC(=O)COO	2.4E7	14500
LABPINCONO2	CC1=CCC(C(C)(CO)(ON(=O)(=O)))CC1	8.7E3	18800

Table S2. Newly implemented Henry's law constants estimated by GROHME, and the temperature-dependence factor $B = \mathrm{d}\ln H_\mathrm{s}/\mathrm{d}(1/T)$ calculated with the method of Kühne et al. (2005). (continued)

compound	**SMILES**	H_s **/ M/atm**	$\mathrm{d}\ln H_\mathrm{s}/\mathrm{d}(1/T)$ **/ K**
Limonene			
C9CONO2	C=C(C)C(CCC(C)=O)CC(=O)(ON(=O)(=O))	8.1E3	19900
LIMALONO2	CC(=O)CCC(CC=O)C(C)(CO)(ON(=O)(=O))	1.3E10	23000
LIMONO2	C=C(C)C(CC=O)CCC(=O)CON(=O)=O	3.9E6	13500
LLIMABONO22	CC(CO)(ON(=O)=O)C1CCC(C)(ON(=O)=O)C(O)C1	3.1E9	18200
LLIMABONO2OOH	CC(CO)(OO)C1CCC(C)(ON(=O)=O)C(O)C1	5.1E11	19200
LLIMABOOH2	CC(CO)(OO)C1CCC(C)(OO)C(O)C1	2.3E14	20200
LLIMABONO2	C=C(C)C1CCC(C)(ON(=O)=O)C(O)C1	8.5E3	12400
LLIMABOOH	C=C(C)C1CCC(C)(OO)C(O)C1	3.6E6	13400
ROO6R1ONO2	CC1(CO)OOC2CC1CCC2(C)ON(=O)=O	1.4E4	15200
ROO6R1OOH	CC1(CO)OOC2CC1CCC2(C)OO	6.9E6	16300
ROO6R5ONO2	CC(=O)CCC(CC(=O)ON(=O)=O)OO	1.7E7	15300
ROO6R5OOH	CC(=O)CCC(CC(=O)OO)OO	4.7E9	16300
ROO6R6ONO2	CC(=O)CCC(CON(=O)=O)OO	6.2E7	12400
ROO6R6OOH	CC(=O)CCC(COO)OO	2.6E10	13500
ROO6R7ONO2	CC(=O)CCC(CO)ON(=O)=O	7.6E6	12800
ROO6R7OOH	CC(=O)CCC(CO)OO	3.3E9	13800
C52COCONO2	CC(=O)CCC(=O)ON(=O)=O	6.8E3	11000
C52COCO3H	CC(=O)CCC(=O)OO	1.9E6	12000
C624ONO2	C=C(COO)C(CO)(CO)ON(=O)=O	2.0E12	18600
C518OOH	C=C(COO)C(=O)CO	4.2E6	14200
C624OOH	C=C(COO)C(CO)(CO)OO	1.2E15	19600
C520ONO2	O=C(CO)C(CO)(COO)ON(=O)=O	2.9E11	20800
BIACETOH2	O=C(CO)C(=O)CO	2.1E8	16700
C520OOH	O=C(CO)C(CO)(COO)OO	5.4E13	21800
Glyoxal oligomers			
GOLIG1	O=CC(O)-O-C(O)C=O	1.5E14	18700
GOLIG2	O=CC(O)-O-C(O)C(O)O	1.5E17	24000
GOLIG3	OC(O)C(O)-O-C(O)C(O)O	3.8E20	28600
Methyl glyoxal oligomers			
MGLYOXDA	CC(=O)C(O)-O-C(O)C(=O)C	2.0E10	15500
MGLYOXDB	CC(=O)C(O)-O-C(O)(C)C(O)(O)	1.5E15	22400
MGLYFA	CC(=O)C(=O)-O-C(O)C(=O)C	4.5E6	15600
MGLYFB	CC(=O)C(=O)-O-C(O)(C)C(O)(O)	7.2E10	22500

5 Additional model output

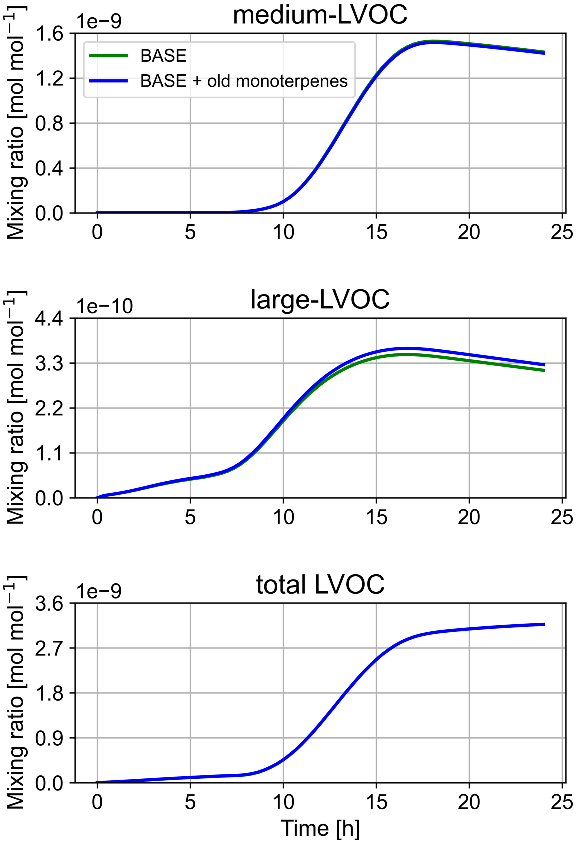

Figure S9. Comparison of the BASE run with a simulation of the BASE run with included carene, camphene and sabinene (old monoterpenes).

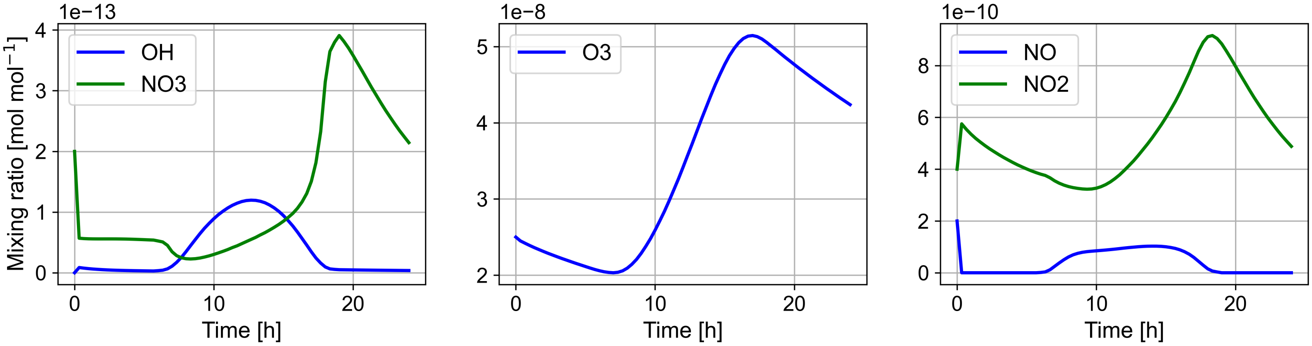

Figure S10. Gas phase mixing ratios of OH, NO_3, NO, NO_2 and O_3 during the BASE (updated mechanism at 298 K) sensitivity run.

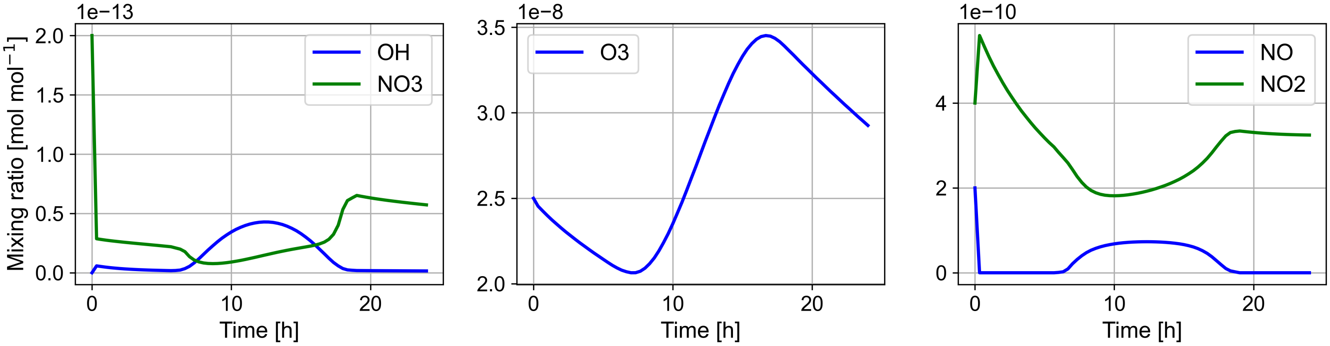

Figure S11. Gas phase mixing ratios of OH, NO_3, NO, NO_2 and O_3 during the BASE-278K sensitivity run.

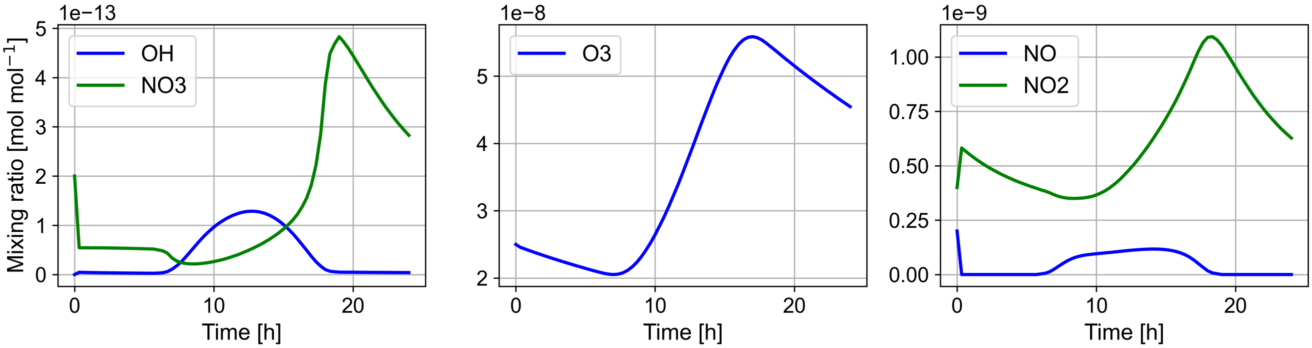

Figure S12. Gas phase mixing ratios of OH, NO_3, NO, NO_2 and O_3 during the OLD sensitivity run.

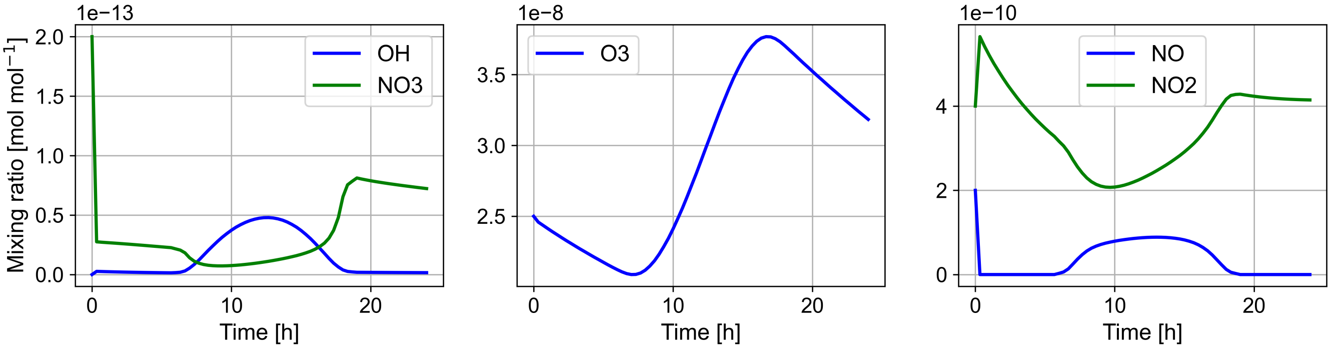

Figure S13. Gas phase mixing ratios of OH, NO_3, NO, NO_2 and O_3 during the OLD-278K sensitivity run.

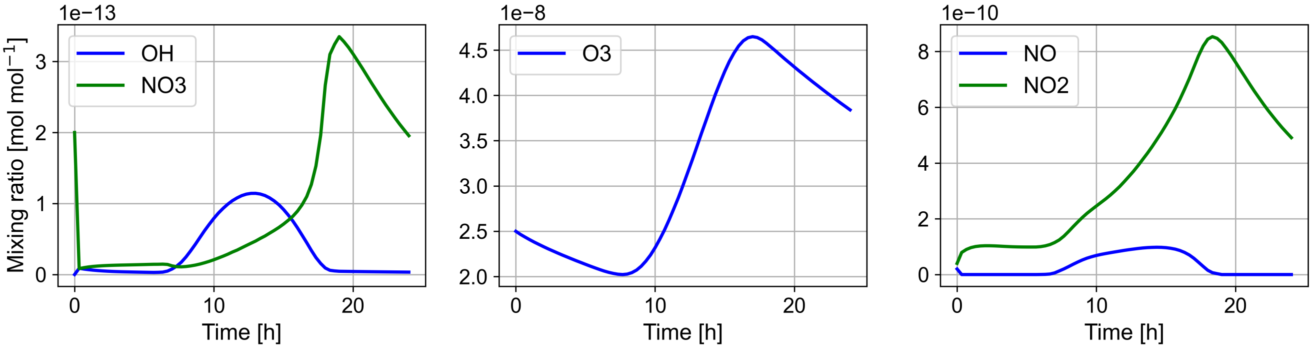

Figure S14. Gas phase mixing ratios of OH, NO_3, NO, NO_2 and O_3 during the low-NOx sensitivity run.

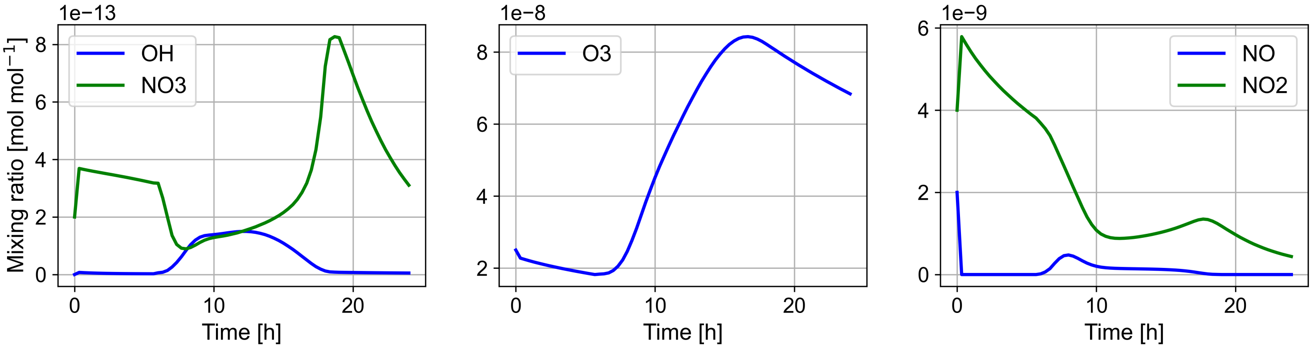

Figure S15. Gas phase mixing ratios of OH, NO_3, NO, NO_2 and O_3 during the medium-NOx sensitivity run.

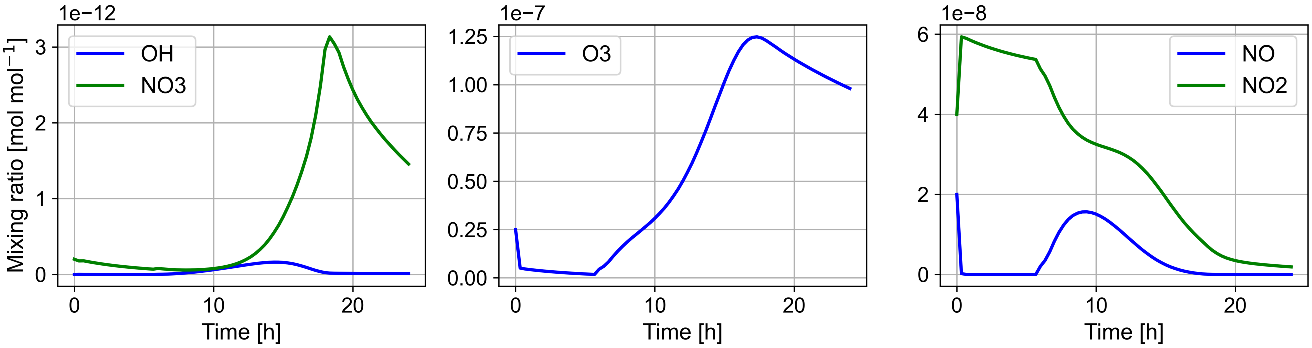

Figure S16. Gas phase mixing ratios of OH, NO_3, NO, NO_2 and O_3 during the high-NOx sensitivity run.

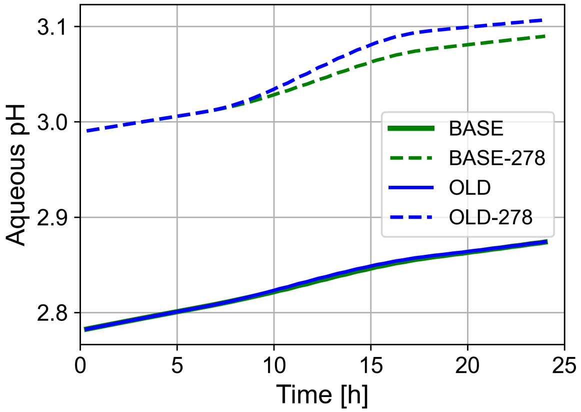

Figure S17. Time dependence of the aqueous pH. The BASE run and the OLD run produce similar acidity's. Thus, their lines overlap. In the SOAS campaign the aerosol pH is approximately 1 (Guo et al., 2015).

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