

Supplement 1

Table S1: JAM3 mechanism additional isoprene oxidation reactions compared to the JAM2 mechanism described in Schultz et al. (submitted).

$\text{C}_5\text{H}_8 + \text{O}_3 \longrightarrow 0.051 \cdot \text{CH}_3\text{O}_2 + 0.1575 \cdot \text{CH}_3\text{CO} + 0.054 \cdot \text{LHMVKABO}_2 + 0.522 \cdot \text{CO} + 0.068750 \cdot \text{HCOOH} + 0.11 \cdot \text{H}_2\text{O}_2 + 0.324750 \cdot \text{MACR} + 0.1275 \cdot \text{C}_3\text{H}_6 + 0.2625 \cdot \text{HO}_2 + 0.255 \cdot \text{CO}_2 + 0.749750 \cdot \text{CH}_2\text{O} + 0.041250 \cdot \text{MACO}_2\text{H} + 0.27 \cdot \text{OH} + 0.244 \cdot \text{MVK}$	$7.86 \cdot 10^{-15} \exp(-1913/\text{T})$	
$\text{LISOPACO}_2 + \text{CH}_3\text{O}_2 \longrightarrow 0.75 \cdot \text{CH}_2\text{O} + 0.75 \cdot \text{LHC}_4\text{ACCHO} + 0.25 \cdot \text{CH}_3\text{OH} + 0.25 \cdot \text{ISOPA}\text{OH} + \text{HO}_2$	$2.4 \cdot 10^{-12}$	products: Tyndall (p.c.)
$\text{LISOPACO}_2 \longrightarrow \text{HO}_2 + \text{HPALD}$	$6.198 \cdot 10^8 \cdot \exp(-7700/\text{T})$	Bulk isomerization (1,6-H-shift) rate constant for all ISOPO2 by Crounse et al. (2011) and adjusted by Fuchs et al. (2013) given as $1.5 * k(\text{ISOPO}_2 + \text{HO}_2) * 2 \cdot 10^{21} \cdot \exp(-9000/\text{T}) \Rightarrow k = 2.05 \cdot 10^{-13} \cdot \exp(1300/\text{T}) \cdot 210^{21} \cdot \exp(-9000/\text{T}) = 6.19810^8 \cdot \exp(-7700/\text{T})$
$\text{ISOPBO}_2 \longrightarrow \text{HO}_2 + \text{HPALD}$	$6.198e + 08 \cdot \exp(-7700./\text{T})$	see note of [LISOPACO2]
$\text{ISOPDO}_2 \longrightarrow \text{HO}_2 + \text{HPALD}$	$6.198e + 08 \cdot \exp(-7700./\text{T})$	see note of [LISOPACO2]
$\text{ISOPBO}_2 \longrightarrow \text{HCHO} + \text{MVK} + \text{OH}$	$3.570e + 13 \cdot \exp(-10770./\text{T})$	1,5-H-shift as in LIM-J by da Silva (2010) and adjusted by Fuchs et al. (2013)
$\text{ISOPDO}_2 \longrightarrow \text{HCHO} + \text{MACR} + \text{OH}$	$1.905e + 13 \cdot \exp(-10570./\text{T})$	1,5-H-shift as in LIM-J by da Silva (2010) and adjusted by Fuchs et al. (2013)
$\text{LIECO}_3 + \text{HO}_2 \longrightarrow 0.6 \cdot \text{LIECO}_3\text{H} + 0.4 \cdot \text{CO}_2 + 0.4 \cdot \text{OH} + 0.25 \cdot \text{LHMVKABO}_2 + 0.15 \cdot \text{MACRO}_2$	$8.207 \cdot 10^{-13} \cdot \exp(980./\text{T})$	k scaled to $2.2 \cdot 10^{-11}$ as recommended by Winiberg ($A = 5.2 \cdot 10^{-13} \cdot 1.578$); cacm products distribution unchanged (Winiberg et al. (2016) and Groß et al. (2014))
$\text{LISOPACO}_2 + \text{LISOPACO}_2 \longrightarrow 1.5 \cdot \text{LHC}_4\text{ACCHO} + \text{HO}_2 + 0.5 \cdot \text{ISOPA}\text{OH}$	$3.350 \cdot 10^{-12}$	k : avg. for primary isoprene RO2 MCM (Jenkin et al. (2003), Tab. 3); products: based on the HOCH2CH2O2 self-reaction (Orlando and Tyndall (2012), Tab.8)
$\text{ISOPBO}_2 + \text{ISOPBO}_2 \longrightarrow 2 \cdot \text{MVK} + 2 \cdot \text{CH}_2\text{O} + 2 \cdot \text{HO}_2$	$6.900 \cdot 10^{-14}$	k : for tertiary isoprene RO2 MCM (Jenkin et al. (2003), Tab. 3)

Table S1: JAM3 mechanism additional isoprene oxidation reactions (continued).

ISOPDO ₂ + ISOPDO ₂ \longrightarrow 1.12 · MACR + 1.12 · CH ₂ O + 1.12 · HO ₂ + 4.800 · 10 ⁻¹² 0.44 · HCOC ₅ + 0.44 · ISOPDOH		k : for secondary isoprene RO ₂ MCM (Jenkin et al. (2003), Tab. 3); products: based on the i-C ₃ H ₇ O ₂ self-reaction (Orlando and Tyndall (2012), Tab.8)
LISOPACO ₂ + ISOPBO ₂ \longrightarrow LHC ₄ ACCHO + 0.75 · MVK + 0.75 · CH ₂ O + 4.808 · 10 ⁻¹³ 1.5 · HO ₂ + 0.25 · ISOPBOH		k : (3.35 · 10 ⁻¹² · 6.9 · 10 ⁻¹⁴) ^{0.5} geometric average of self-reaction k_s (arbitrary estimate by Madronich and Calvert (1990))
LISOPACO ₂ + ISOPDO ₂ \longrightarrow 0.75 · LHC ₄ ACCHO + 0.5 · MACR + 4.010 · 10 ⁻¹² 0.5 · CH ₂ O + HO ₂ + 0.25 · ISOPAOH + 0.25 · HCOC ₅ + 0.25 · ISOPDOH		k : (3.35 · 10 ⁻¹² · 4.8 · 10 ⁻¹²) ^{0.5} geometric average of self-reaction k (arbitrary estimate by Madronich and Calvert (1990))
ISOPBO ₂ + ISOPDO ₂ \longrightarrow 0.75 · MVK + 0.75 · MACR + 1.5 · CH ₂ O + 5.755 · 10 ⁻¹³ 1.5 · HO ₂ + 0.25 · ISOPBOH + 0.25 · HCOC ₅		k : (6.9 · 10 ⁻¹⁴ · 4.8 · 10 ⁻¹²) ^{0.5} geometric average of self-reaction k (arbitrary estimate by Madronich and Calvert (1990))
LHC ₄ ACCO ₃ \longrightarrow HO ₂ + PACALD	1.230 · 10 ⁹ · exp(-6186/T)	1,6-H-shift (not bulk!) rate constant for the Z41 isomer as in SI Taraborrelli et al. (2012) 2012
LHC ₄ ACCO ₃ + HO ₂ \longrightarrow 0.37 · LHC ₄ ACCO ₃ H + 0.12 · LHC ₄ ACCO ₂ H + 8.207 · 10 ⁻¹³ · exp(980/T) 0.12 · O ₃ + 0.51 · CO ₂ + 0.51 · OH + 0.255 · HYAC + 0.255 · GLYALD + 0.255 · CH ₃ CO + 0.255 · CO + 0.255 · HO ₂		k scaled to 2.2 · 10 ⁻¹¹ as recommended by Winiberg ($A = 5.2 \cdot 10^{-13} \cdot 1.578$) ; product distribution in analogy to CH ₃ CO ₃ + HO ₂ reactions (Winiberg et al. (2016) and Groß et al. (2014))

Table S2: JAM3 mechanism: ISOPOOH reactions.

$\text{LISOPACOOH} + \text{OH} \longrightarrow 0.415 \cdot \text{LIEPOX} + 0.415 \cdot \text{OH} + 1.54 \cdot 10^{-10}$ $0.415 \cdot \text{LISOPOOHO}_2 + .14 \cdot \text{LHC}_4\text{ACCHO} + 0.03 \cdot \text{H}_2\text{O} + 0.03 \cdot \text{LISOPACO}_2$	<p>k from MCMv3.3.1 and OH-addition branching ratios estimated with site-specific SAR by Peeters et al. (2007) and H-abstraction channel assumed to be like the one for CH₃OOH + OH reaction and abstraction from the alpha-hydroperoxyl allyl hydrogen estimated by SAR of MOM (Taraborrelli in prep.) being $2.12 \cdot 10^{-11}$</p>
$\text{ISOPBOOH} + \text{OH} \longrightarrow 0.63 \cdot \text{LIEPOX} + 0.63 \cdot \text{OH} + 0.12 \cdot \text{LISOPOOHO}_2 + 7.5 \cdot 10^{-11}$ $0.15 \cdot \text{H}_2\text{O} + 0.15 \cdot \text{ISOPBO}_2$	<p>St. Clair et al. (2015)</p>
$\text{ISOPDOOH} + \text{OH} \longrightarrow 0.79 \cdot \text{LIEPOX} + 0.79 \cdot \text{OH} + 0.14 \cdot \text{LISOPOOHO}_2 + 1.18 \cdot 10^{-10}$ $0.07 \cdot \text{H}_2\text{O} + 0.07 \cdot \text{ISOPDO}_2$	<p>St. Clair et al. (2015)</p>

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