Supplement 1

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

Reaction	Rate	Note
$C_5H_8 + O_3 \longrightarrow 0.051 \cdot CH_3O_2 + 0.1575 \cdot CH_3CO + 0.054 \cdot LHMVKABO_2 + 0.522 \cdot CO + 0.068750 \cdot HCOOH + 0.11 \cdot H_2O_2 + 0.324750 \cdot MACR + 0.1275 \cdot C_3H_6 + 0.2625 \cdot HO_2 + 0.255 \cdot CO_2 + 0.749750 \cdot CH_2O + 0.041250 \cdot MACO_2H + 0.27 \cdot OH + 0.244 \cdot MVK$	$7.86 \cdot 10^{-15} \exp(-1913/T)$	
$LISOPACO_2 + CH_3O_2 \longrightarrow 0.75 \cdot CH_2O + 0.75 \cdot LHC_4ACCHO + 0.25 \cdot CH_3OH + 0.25 \cdot ISOPAOH + HO_2$	$2.4 \cdot 10^{-12}$	products: Tyndall (p.c.)
$LISOPACO_2 \longrightarrow HO_2 + HPALD$	$6.198 \cdot 10^8 \cdot \exp(-7700/T)$	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 $1.5 * k(ISOPO2 + HO2) * 2 \cdot 10^{21} \cdot \exp(-9000/T) => k = 2.05 \cdot 10^{-13} \cdot \exp(1300/T) \cdot 210^{21} \cdot \exp(-9000/T) = 6.19810^8 \cdot \exp(-7700/T)$
$ISOPBO_2 \longrightarrow HO_2 + HPALD$	$6.198e + 08 \cdot \exp(-7700./T)$	see note of [LISOPACO2]
$ISOPDO_2 \longrightarrow HO_2 + HPALD$	$6.198e + 08 \cdot \exp(-7700./T)$	see note of [LISOPACO2]
$ISOPBO_2 \longrightarrow HCHO + MVK + OH$	$3.570e + 13 \cdot \exp(-10770./T)$	1,5-H-shift as in LIM-J by da Silva (2010) and adjusted by Fuchs et al. (2013)
$ISOPDO_2 \longrightarrow HCHO + MACR + OH$	$1.905e + 13 \cdot \exp(-10570./T)$	1,5-H-shift as in LIM-J by da Silva (2010) and adjusted by Fuchs et al. (2013)
$LIECO_3 + HO_2 \longrightarrow 0.6 \cdot LIECO_3H + 0.4 \cdot CO_2 + 0.4 \cdot OH + 0.25 \cdot LHMVKABO_2 + 0.15 \cdot MACRO_2$	$8.207 \cdot 10^{-13} \cdot \exp(980./T)$	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))
$LISOPACO_2 + LISOPACO_2 \longrightarrow 1.5 \cdot LHC_4ACCHO + HO_2 + 0.5 \cdot ISOPAOH$	$3.350 \cdot 10^{-12}$	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)
$ISOPBO_2 + ISOPBO_2 \longrightarrow 2 \cdot MVK + 2 \cdot CH_2O + 2 \cdot HO_2$	$6.900 \cdot 10^{-14}$	k: for tertiary isoprene RO2 MCM (Jenkin et al. (2003), Tab. 3)

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

Reaction	k	Notes
$ISOPDO_2 + ISOPDO_2 \longrightarrow 1.12 \cdot MACR + 1.12 \cdot CH_2O + 1.12 \cdot HO_2 + 0.44 \cdot HCOC_5 + 0.44 \cdot ISOPDOH$	$4.800 \cdot 10^{-12}$	k : for secondary isoprene RO2 MCM (Jenkin et al. (2003), Tab. 3); products: based on the i-C3H7O2 self-reaction (Orlando and Tyndall (2012), Tab.8)
$LISOPACO_2 + ISOPBO_2 \longrightarrow LHC_4ACCHO + 0.75 \cdot MVK + 0.75 \cdot CH_2O + 1.5 \cdot HO_2 + 0.25 \cdot ISOPBOH$	$4.808 \cdot 10^{-13}$	k : $(3.35 \cdot 10^{-12} \cdot 6.9 \cdot 10^{-14})^{0.5}$ geometric average of self-reaction ks (arbitrary estimate by Madronich and Calvert (1990))
$LISOPACO_2 + ISOPDO_2 \longrightarrow 0.75 \cdot LHC_4ACCHO + 0.5 \cdot MACR + 0.5 \cdot CH_2O + HO_2 + 0.25 \cdot ISOPAOH + 0.25 \cdot HCOC_5 + 0.25 \cdot ISOPDOH$	$4.010 \cdot 10^{-12}$	k : $(3.35 \cdot 10^{-12} * 4.8 \cdot 10^{-12})^{0.5}$ geometric average of self-reaction k (arbitrary estimate by Madronich and Calvert (1990))
$ISOPBO_2 + ISOPDO_2 \longrightarrow 0.75 \cdot MVK + 0.75 \cdot MACR + 1.5 \cdot CH_2O + 1.5 \cdot HO_2 + 0.25 \cdot ISOPBOH + 0.25 \cdot HCOC_5$	$5.755 \cdot 10^{-13}$	k : $(6.9 \cdot 10^{-14} \cdot 4.8 \cdot 10^{-12})^{0.5}$ geometric average of self-reaction k (arbitrary estimate by Madronich and Calvert (1990))
$LHC_4ACCO_3 \longrightarrow HO_2 + PACALD$	$1.230 \cdot 10^9 \cdot \exp(-6186/T)$	1,6-H-shift (not bulk!) rate constant for the Z41 isomer as in SI Taraborrelli et al. (2012) 2012
$LHC_4ACCO_3 + HO_2 \longrightarrow 0.37 \cdot LHC_4ACCO_3H + 0.12 \cdot LHC_4ACCO_2H + 0.12 \cdot O_3 + 0.51 \cdot CO_2 + 0.51 \cdot OH + 0.255 \cdot HYAC + 0.255 \cdot GLYALD + 0.255 \cdot CH_3CO + 0.255 \cdot CO + 0.255 \cdot HO_2$	$8.207 \cdot 10^{-13} \cdot \exp(980/T)$	k scaled to $2.2 \cdot 10^{-11}$ as recommended by Winiberg ($A = 5.2 \cdot 10^{-13} \cdot 1.578$) ; product distribution in analogy to $CH_3CO_3 + HO_2$ reactions (Winiberg et al. (2016) and Groß et al. (2014))

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