Supplementary Material

NO_x emissions, isoprene oxidation pathways, vertical mixing, and implications for surface ozone in the Southeast United States

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Table S1 – Species Added to GEOS-Chem

Species	**Note**
HPALD	Hydroperoxyaldehydes ($C_5H_8O_3$)
HC187	Epoxide oxidation product m/z 187-189
DHDN	C_5 dihydroxydinitrate

Table S2 – Reaction Rates and Productions Updated in GEOS-Chem

Reaction	**Reference**	**Rate Constant**	**Reference**
$RIO_2 + HO_2 \rightarrow 0.937RIP + 0.063OH + 0.025MACR + 0.038MVK + 0.063HO_2 + 0.063CH_2O$	(Liu et al., 2013)	2.06E-13*exp(1300/T)	(Saunders et al., 2003)
$RIO_2 + NO \rightarrow 0.91NO_2 + 0.82HO_2 + 0.82CH_2O + 0.476MVK + 0.344MACR + 0.058HC_5 + 0.03DIBOO + 0.009ISOPND + 0.081ISOPNB$	(Liu et al., 2013;Fisher et al., 2016)	2.7E-12*exp(350/T)	(Paulot et al., 2009a)
$RIO_2 \rightarrow HO_2 + HPALD$	(Peeters et al., 2009;Peeters and Muller, 2010;Crounse et al., 2011)	4.07E8*exp(-7694/T)	Rate adjusted by Crounse et al. (2011)
$RIO_2 + RIO_2 \rightarrow 0.91HO_2 + 0.75CH_2O + 0.45MVK + 0.29MACR + 0.09DIBOO + 1.11HC5 + 0.29CO$	(Xie et al., 2013)	2.3E-12	(Xie et al., 2013)
$HPALD + OH \rightarrow MGLY + CO + CH_2O + OH$	(Squire et al., 2015)	5.1E-11	(Wolfe et al., 2012)
$HPALD + h\upsilon \rightarrow OH + HO_2 + 0.5GLYC +$	(Stavrakou et al., 2010)	Rate is equivalent to	(Peeters and Muller,

0.25 GLYX + 0.25MGLY + CH$_2$O + 0.5 HAC		MACR photolysis	2010)
ISOPND + OH → 0.1IEPOX + 0.9 ISOPNDO$_2$ + 0.1NO$_2$	(Jacobs et al., 2014)	1.2E-11*exp(652/T)	(Lee et al., 2014)
ISOPNB + OH → 0.1IEPOX + 0.90ISOPNBO$_2$ + 0.1NO$_2$	(Jacobs et al., 2014)	2.4E-12*exp(745/T)	(Lee et al., 2014)
ISOPNDO$_2$ + NO ➔ 0.019MACRN + 0.057HCOOH + 0.27HAC + 0.210ETHLN + 0.15CH$_2$O + 0.790NO$_2$ + 0.3GLYC + 0.3PROPNN + 0.61HO$_2$ + 0.27DHDN + 0.075MVKN + 0.057ISOPNDO$_2$ (a)	(Lee et al., 2014)	2.4E-12*exp(360/T)	(Lee et al., 2014)
ISOPNBO$_2$ + NO ➔ 0.09GLYC + 0.09HAC + 0.69CH2O + 0.44MACRN + 0.69HO$_2$ + 0.26MVKN + 0.88NO$_2$ + 0.21DHDN	(Lee et al., 2014)	2.4E-12*exp(360/T)	(Lee et al., 2014)
ISOPNDO$_2$ + HO$_2$ ➔0.01MACRN + 0.2HAC + 0.2ETHLN + 0.07CH$_2$O + 0.23GLYC + 0.23PROPNN + 0.5HO$_2$ + 0.5OH + 0.06MVKN + 0.5ISNP (b)	(Lee et al., 2014)	8.7E-14*exp(1650/T)	(Lee et al., 2014)
ISOPNBO$_2$ + HO$_2$ ➔ 0.06GLYC + 0.06HAC + 0.44CH$_2$O + 0.28MACRN + 0.16MVKN + 0.06NO$_2$ + 0.44HO$_2$ + 0.5OH + 0.5ISNP (b)	(Lee et al., 2014)	8.7E-14*exp(1650/T)	(Lee et al., 2014)
ISOPND + O$_3$ → 0.06NO$_2$ + 0.37OH + 0.24PROPNN + 0.26ETHLN + 0.26HAC + 0.24GLYC + 0.63CO$_2$ + 0.24MOH + 0.09EOH + 0.2CH$_2$O + 0.1MCO3 + 0.06GLYX + 0.16HAC + 0.14PROPNN + 0.3HNO$_3$(d)	(Lee et al., 2014)	2.9E-17	(Lee et al., 2014)
ISOPNB + O$_3$ → 0.05HO2 + 0.05OH + 0.11MVKN + 0.32MACRN + 0.16HCOOH + 0.62CH2O + 0.36CO2 + 0.21CO + 0.06PROPNN + 0.36PROPNN(c) + 0.1MVKN + 0.41HNO3(d)	(Lee et al., 2014)	3.7E-19	(Lee et al., 2014)
IEPOX + OH ➔ IEPOXOO	(Paulot et al., 2009b)	4.82E-11*exp(-400/T)(e)	(Bates et al., 2014)
IEPOXOO + HO$_2$ → 0.085HAC + 0.025GLYC + 0.085GLYX + 0.085MGLY + 1.125OH + 0.825HO$_2$ + 1.1CO$_2$ + 0.375CH2O + 0.278HCOOH + 0.6CO + 0.44HC187(f)	(Bates et al., 2014)	2.06E-13*exp(1300/T)	(Paulot et al., 2009b)
IEPOXOO + NO → 0.117HAC + 0.088GLYC + 0.088GLYX + 0.088MGLY + 0.125OH + 0.825HO$_2$ + 0.8CO$_2$ + 0.375CH$_2$O + 0.142HCOOH + 0.678CO + NO$_2$ + 0.473HC187(f)	(Bates et al., 2014)	2.7E-12exp*(350/T)	(Paulot et al., 2009b)
HC187 + OH ➔ 0.5MCO$_3$ + 0.5MGLY + 0.5HO$_2$ + 0.5CO + CH$_2$O	(Bates et al., 2014)	1.4E-11	(Bates et al., 2014)

(a) The yields are not identical to the Lee et al. (2014) values and there is artificial recycling of ISOPNDO$_2$ to account for non-unity reactants (i.e. in Lee et al. (2014) one ISOPNDO$_2$ reacts with 1.06ISOPNDO$_2$).

(b) In Lee et al. (2014), a C5 hydroperoxide is formed (ROOH). In order to close the nitrogen budget this would have to be ISNP – a peroxide species with a nitrate group.

(c) Replace C4NACID in Lee et al. (2014) with PROPNN.

(d) HNO$_3$ added to this reaction to close the nitrogen budget, as we replace ethyl nitrate with its oxidation product, peroxyacetyl nitrate.

(e) Update pre-exponential factor of this reaction in globchem.dat from Bates et al. (2014).

(f) Other organic products were identified by Bates et al. (2014). These structural isomers are replaced with CO for the epoxide product (m/z 201) and a new species (also added as a tracer) is added to GEOS-Chem to account for the m/z 187 and 189 isomers.

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