

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 ₅ H ₈ O 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
$\text{RIO}_2 + \text{HO}_2 \rightarrow 0.937\text{RIP} + 0.063\text{OH} + 0.025\text{MACR} + 0.038\text{MVK} + 0.063\text{HO}_2 + 0.063\text{CH}_2\text{O}$	(Liu et al., 2013)	$2.06\text{E-}13 \cdot \exp(1300/T)$	(Saunders et al., 2003)
$\text{RIO}_2 + \text{NO} \rightarrow 0.91\text{NO}_2 + 0.82\text{HO}_2 + 0.82\text{CH}_2\text{O} + 0.476\text{MVK} + 0.344\text{MACR} + 0.058\text{HC}_5 + 0.03\text{DIBOO} + 0.009\text{ISOPND} + 0.081\text{ISOPNB}$	(Liu et al., 2013; Fisher et al., 2016)	$2.7\text{E-}12 \cdot \exp(350/T)$	(Paulot et al., 2009a)
$\text{RIO}_2 \rightarrow \text{HO}_2 + \text{HPALD}$	(Peeters et al., 2009; Peeters and Muller, 2010; Crouse et al., 2011)	$4.07\text{E}8 \cdot \exp(-7694/T)$	Rate adjusted by Crouse et al. (2011)
$\text{RIO}_2 + \text{RIO}_2 \rightarrow 0.91\text{HO}_2 + 0.75\text{CH}_2\text{O} + 0.45\text{MVK} + 0.29\text{MACR} + 0.09\text{DIBOO} + 1.11\text{HC}_5 + 0.29\text{CO}$	(Xie et al., 2013)	2.3E-12	(Xie et al., 2013)
$\text{HPALD} + \text{OH} \rightarrow \text{MGLY} + \text{CO} + \text{CH}_2\text{O} + \text{OH}$	(Squire et al., 2015)	5.1E-11	(Wolfe et al., 2012)
$\text{HPALD} + h\nu \rightarrow \text{OH} + \text{HO}_2 + 0.5\text{GLYC} +$	(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 + 0.69CH ₂ O + 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 + 0.1MCO ₃ + 0.06GLYX + 0.16HAC + 0.14PROPNN + 0.3HNO ₃ ^(d)	(Lee et al., 2014)	2.9E-17	(Lee et al., 2014)
ISOPNB + O ₃ → 0.05HO ₂ + 0.05OH + 0.11MVKN + 0.32MACRN + 0.16HCOOH + 0.62CH ₂ O + 0.36CO ₂ + 0.21CO + 0.06PROPNN + 0.36PROPNN ^(c) + 0.1MVKN + 0.41HNO ₃ ^(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 + 0.375CH ₂ O + 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 ISOPNDO₂ to account for non-unity reactants (i.e. in Lee et al. (2014) one ISOPNDO₂ reacts with 1.06ISOPNDO₂).

^(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) HNO₃ 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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