Supporting information for "Aqueous-phase Secondary Organic Aerosol and Organosulfate Formation in Atmospheric Aerosols: A Modeling Study"

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I. Model specifics

Table S1. List of gas-phase species

Molecular formula	Abbreviation	Name	Note[a]
O3		Ozone	
O(^{1}D)	O1D	^{1}D oxygen atom	
O(^{3}P)	O3P	^{3}P oxygen atom	
H2O2		Hydrogen peroxide	
OH		Hydroxy radical	
HO2		Hydroperoxyl radical	
NO		NO radical	
NO2		Nitrogen dioxide	
NO3		Nitrate radical	
N2O5		Dinitrogen pentoxide	
HNO3		Nitric acid	
HONO		Nitrous acid	
HNO4		Pernitric acid	
SO2		Sulfur dioxide	
CO		Carbon monoxide	
HCHO	FORM	Formaldehyde	
CH3O		Methoxy radical	
CH3OH		Methanol	
CH2O2	FORMIC	Formic acid	
CH3O2		Methylperoxy radical	
CH3O2H		Methylhydrogen peroxide	
C2H2		Acetylene	
C2H4O2	GLYC	Glycolaldehyde	
C2H2O2	GLYX	Glyoxal	
C2H4O2	ACETIC	Acetic acid	
C2H4O3	GLYCAC	Glycolic acid	
C2H2O3	GLYAC	Glyoxylic acid	
CH3CO3		Acetylperoxy radical	
C2H2O4	OXLAC	Oxalic acid	
C2H3NO4	ETHLN	Ethanal nitrate	H
C3H5NO4	PROPNN	Propanone nitrate	H
C2H3NO5	PAN	Peroxyacetyl nitrate	
C3H4O2	MGLY	Methylglyoxal	
C3H6O2	HAC	Hydroxyacetone	
C3H4O3	PYRAC	Pyruvic acid	
	HC4	C4 alkane	H
C4H6O	MACR	Methacrolein	
C4H6O	MVK	Methylvinylketone	
C4H4O3	EPXC4DIAL	C4 epoxy dial	
C4H5O3	MACP	MACR peroxy radical	
C4H5O3	MVKP	MVK peroxy radical	
C4H3O4	TCO3	H(CO)CH=CHCO3, peroxy radical formed from DCB photolysis	b
C4H7NO5	MVKN	MVK nitrate	H
C4H7NO5	MACRN	MACR nitrate	H
C4H9NO7	DHBN	Dihydroxybutanone nitrate	H
C5H8	ISOP	Isoprene	
C5H6O	MF	Methylfuran	H

C5H8O2	HC5	4-hydroxy-2-methyl-but-2-enal	
C5H6O3	MOBA	2-methyl-4-oxobut-2-enoic acid	H
C5H6O3	EPXMC4DIAL	methyl C4 epoxy dial	
C5H9O3	ISOPOO	Isoprene hydroxyhydroperoxyl radical	
C5H10O3	ISOPOOH	Isoprene hydroxyhydroperoxide	L
C5H10O3	IEPOX	Isoprene-derived dihydroxyepoxide	L
C5H7O4	HC5OO	HC5 peroxy radical	
C5H8O4	DHMOB	2,4-dihydroxy-2-methyl-3-oxobutanal	H
C5H9O4	DIBOO	Dibble peroxy radical	H
C5H10O5	IEPOXOO	IEPOX peroxy radical	L
C5H5O5	MOBAOO	Peroxy radical formed from MOBA	H
C5H9O7	ISOPNOOd	Peroxy radical formed from ISOPNd	H
C5H9O7	ISOPNOOb	Peroxy radical formed from ISOPNb	H
C5H9NO4	ISOPNd	Isoprene nitrate	H
C5H9NO4	ISOPNb	Isoprene nitrate	H
C7H8	TOL	Toluene	
C7H8O	CSL	Cresol	
C7H8O3	TOL_EPOX	2,3-epoxy-6-oxo-heptenal	
C8H10	XYL	Xylenes	
C8H10O	MCSL	Dimethyl phenols (methylcresols)	
C8H10O3	XYL_EPOX	Xylene-derived epoxide	
	ALD	Acetaldehyde and higher aldehydes	b
	OP2	Higher peroxides	b
	XO2	Other peroxides (Accounts for additional NO to NO conversions affected by the lumped organic species)	b
	DCB	Unsaturated dicarbonyl	b
	KET	Ketones	b
	OLI	Internal alkenes	L, b
	OLT	Terminal alkenes	b
	OLTP	Peroxy radical formed from OLT	b
	HC3P	Peroxy radical formed from OP2 + OH	b
	OLIP	Peroxy radical formed from OLI	b
	KETP	Peroxy radical formed from KET	b
	ETHP	Peroxy radical formed from ketone photolysis	b
	ONIT	Organic nitrate	b
	APN	Higher acyl peroxy nitrates	
	FURANONES	Furanones formed from oxidation of aromatics	
	AROMATIC_KETONES	Aromatic ketones formed from oxidation of aromatics	
	UNSAT_ALDEHYDES	Unsaturated aldehydes primarily formed from oxidation of aromatics	
	POLYFXNAL AROMATICS	Polyfunctional aromatics	

a. L = Low-NOx scheme only, H = high-NOx scheme only
b. See Lim et al. (2005)

Table S2. List of aqueous-phase species

Molecular formula	Abbreviation	Name	Note[a]
HO2		Hydroperoxyl radical	
H2O2		Hydrogen peroxide	
OH		Hydroxy radical	
O2-		superoxide	
HSO4-	bisulfate	Bisulfate ion	
SO4-2	sulfate	Sulfate ion	
SO4-		Sulfate radical	
HSO4-	HSO4rad	Bisulfate radical	
H2SO4		Sulfuric acid	
CO2		Carbon dioxide	
CO		Carbon monoxide	
CO2-		Carbon dioxide anion	
HCO3-		Bicarbonate (I) ion	
CO3-2		Carbonate (II) ion	
CO3-		Carbonate radical	
NO3-		Nitrate (I) ion	
NO2-		Nitrite (I) ion	
CH2O	FORM	Formaldehyde	
CH2OH		Hydroxymethyl	
HCO2-	FORMIC-	Formate ion	
COOH		Carboxyl radical	
HCO2H	FORMIC	Formic acid	
CHOHOH		Hydrated formaldehyde radical	
C2H3O2	GLYCR1	Glycolaldehyde radical 1	
C2H3O2	GLYCR2	Glycolaldehyde radical 2	
C2H4O2	GLYC	Glycolaldehyde	
CH3CO2-		Acetate ion	
CH3CO2H		Acetic acid	
C2O3-	GLYACR-	Glyoxylic acid radical-	
C2HO3	GLYACR	Glyoxylic acid radical	
C2HO3-	GLYAC-	Glyoxylate ion	
C2H2O3	GLYAC	Glyoxylic acid	
C2H2O3-	GLYCACR-	Glycolic acid radical-	
C2H3O3	GLYCACR	Glycolic acid radical	
C2H3O3-	GLYCAC-	Glycolate (I) ion	
C2H4O3	GLYCAC	Glycolic acid	
C2O4-2	OXLAC--	Oxalate (II) ion	
C2HO4-	OXLAC-	Oxalate (I) ion	
C2H2O4	OXLAC	Oxalic acid	
C2H3O4	GLYCR1O2	Glycolaldehyde peroxy radical 1	
C2H3O4	GLYCR2O2	Glycolaldehyde peroxy radical 2	
C2H5O4	GLYR	Glyoxal radical	
C2H6O4	GLYX	Glyoxal (hydrated)	
C2O5-	GLYACRO2-	Glyoxylic acid peroxy radical-	
C2HO5	GLYACRO2	Glyoxylic acid peroxy radical	
C2H3O5	GLYCACRO2	Glycolic acid peroxy radical	
C2H5O6	GLYRO2	Glyoxal peroxy radical	
C2H2O6S	GLYOS	Organosulfate formed from GLYX	
C2H4O6S	GLYCOS	Organosulfate formed from GLYC	
C2H2O7S	GLYACOS	Organosulfate formed from GLYAC	

C2H4O7S	GLYCACOS	Organosulfate formed from GLYCAC	
C3H3O3-	PYRAC-	Pyruvate (I) ion	
C3H4O3	PYRAC	Pyruvic acid	
C3H3O4	MArad	Malonic acid radical	
C3H3O6	MAradO2	Malonic acid radical	
C3H4O4	MALONIC	Malonic acid	
C3H6O6	MGLY	Methylglyoxal (hydrated)	
	X	Malonic acid oxidation product	
C4H6O	MACR	Methacrolein	
C4H6O	MVK	Methylvinylketone	
C4H4O3	EPXC4DIAL	C4 epoxy dial	
C4H5O4	SArad	Succinic acid radical	
C4H6O4	SUCCINIC	Succinic acid	
C4H6O4	EPXC4DIAL diol	Diol formed from EPXC4DIAL	
C4H5O6	SAradO2	Succinic acid peroxy radical	
	Y	Succinic acid oxidation product	
C4H6O7S	EPXC4DIAL OS	Organosulfate formed from EPXC4DIAL	
	MVKOS	Organosulfates formed from MVK + SO4-	b
	MACROS	Organosulfates formed from MACR+ SO4-	b
C5H8	ISOP	Isoprene	
C5H6O3	EPXMC4DIAL	Methyl C4 epoxy dial	
C5H8O4	EPXMC4DIAL diol	Diol formed from EPXMC4DIAL	
C5H8O7S	EPXMC4DIAL OS	Organosulfate formed from EPXMC4DIAL	
C5H10O3	IEPOX	Isoprene-derived epoxydiol	L
C5H12O4	tetrol	2-methyltetrol	L
C5H12O7S	IEPOXOS	Organosulfate formed from IEPOX	L
	ISOPOS	Organosulfates formed from ISOP + SO4-	b
C7H6O3	TOL_EPOX	2,3-epoxy-6-oxo-heptenal	
C7H8O4	TOL_EPOX diol	Diol formed from TOL_EPOX	
C7H8O7S	TOL_EPOX OS	Organosulfate formed from TOL_EPOX	
C8H10O3	XYL_EPOX	Xylene-derived epoxide	
C8H12O4	XYL_EPOX diol	Diol formed from XYL_EPOX	
C8H12O7S	XYL_EPOX OS	Organosulfate formed from XYL_EPOX	
	ALD	Acetaldehyde and higher aldehydes	
	UNSAT_ALDEHYDES	Unsaturated aldehydes, primarily formed from aromatics oxidation	

a. L = Low-NOx scheme only, H = high-NOx scheme only
b. see Noziere et al. (2010) for molecular formulae, structures

Table S3. Effective Henry's Law constants (H*) and accommodation coefficients (α)

Species	H* (M/atm)	α	Reference
HO2	$H^* = exp\left(-\frac{\Delta G}{RT}\right) * \left(1 + \frac{2.05 \times 10^{-5}}{10^{-pH}}\right)$ $\Delta G = -4.19 + 0.023 * (298 - T)$ kcal/mol	1	(*1*,*2*)
MACR	6.5	0.02	(*3*) a
MVK	41	0.02	(*3*) a
IEPOX	1.9e7	0.02	(*4*) a
GLYC	4.14e4	0.023	(*5*,*6*) g
GLYX	1e8	0.023	(*7*,*8*)
MGLY	3.71e3	0.023	(*5*,*6*) g
H2O2	exp(6621/T-11.0)	0.11	(*8*,*9*)
OH	29.7	0.05	(*8*,*10*)
FORM	2.97e3	0.02	(*5*,*8*)
FORMIC	5530	0.012	(*8*,*11*,*12*)
GLYCAC	2.83e4	0.019	(*6*,*13*) b
GLYAC	1e4	0.019	(*6*,*13*) b
PYRAC	exp(-4.41706+5087.92/T)	0.019	(*6*,*11*) b
OXLAC	5e8	0.019	(*6*,*14*) b
ACETIC	5500	0.019	(*8*,*11*,*12*)
CO2	4.58e-2	2e-4	(*8*,*15*)
CH3OH	220	0.015	(*8*,*12*,*16*)
CH3OOH	300	0.0038	(*8*,*12*,*16*)
ISOP	0.028	1e-4	(*16*) a
N2O5	1.4e10	0.005	(*6*,*17*,*18*)
HNO3	2.1e5	0.2	(*8*,*19*,*20*)
HONO	50	0.0028	(*8*,*10*,*21*)
HNO4	1e5	0.2	(*8*) c
TOL_EPOX	2.5e5	0.02	(*22*) a,d
UNSAT_ALDEHYDES	2.5e4	0.02	(*22*) a,e
EPXC4DIAL	1.4e5	0.02	(*22*) a,d
ALD	11.4	0.03	(*5*,*8*) f
XYL_EPOX	1.09e5	0.02	(*22*) a,d
EPXC4MDIAL	2.478e4	0.02	(*22*) a,d

a. Estimated accommodation coefficient
b. Assume accommodation coefficient same as acetic acid
c. Assume accommodation coefficient same as HNO3
d. Henry's law constant estimated using SPARC (*22*)
e. Henry's law constant estimated based on O=CC=CC(=O)C using SPARC (*22*)
f. Henry's law, accommodation coefficient values for acetaldehyde.
g. Assume accommodation coefficient same as glyoxal

Table S4. Gas-phase photolysis reactions

Reaction	Rate[a] (s^{-1})	Note[b]
H2O2 + hν → 2 OH	7.66e-6	
O3 + hν → O1D + O2	3.55e-5	
O3 + hν → O3P + O2	2.08e-4	
NO2 + hν → NO + O3P	8.79e-3	
NO3 + hν → NO2 + O3P	1.53e-1	
NO3 + hν → NO + O2	2.21e-2	
HNO3 + hν → NO2 + OH	6.56e-7	
HONO + hν → NO + OH	1.95e-3	
N2O5 + hν → NO2 + NO3	2.54e-5	
FORM + hν → H2 + CO	4.85e-5	
FORM + hν → 2 HO2 + CO	3.16e-5	c
GLYX + hν → 0.13 FORM + 1.87 CO	5.55e-5	c
GLYX + hν → 0.45 FORM + 1.55 CO + 0.80 HO2	2.71e-5	c
MGLY + hν → CH3CO3 + CO + HO2	1.24e-4	c
GLYC + hν → FORM + CO + 2 HO2	1.93e-5	c
ALD + hν → CH3OO + HO2 + CO	4.62e-6	c, d
HC5 + hν → CH3CO3 + GLYC + HO2 + CO	8.30e-6	
HC5 + hν → OP2 + HO2	8.30e-6	
MACR + hν → 1.65 CO + HO2 + 0.35 CH3CO3 + FORM + 0.65 CH3OO	8.30e-6	e
MACR + hν → OP2 + HO2	8.30e-6	
MVK + hν → 0.5 CH3CO3 + 0.5 HCHO + 0.5 HO2 + CO + 0.5C3H6	2.68e-5	
HAC + hν → CH3CO3 + HCHO + HO2	3.83e-6	
OP2 + hν → ALD + HO2 + OH	9.26e-6	
KET + hν → CH3CO3 + ETHP	1.40e-6	
DCB + hν → 0.98HO2 + TCO3 + 0.02CH3CO3	6.04e-4	L
organic nitrates (ISOPNd+ISOPNb+ISOPNOOd+DHBN+PROPNN+ MVKN+ETHLN+ISOPNOOb+MACRN+ONIT) + hν → 0.2 ALD + 0.8 KET + HO2 + NO2	1.47e-6	
MOBA + hν → GLYAC + HO2 + CO +CH3O2	8.30e-6	H
TOL_EPOX + hν → 0.5 EPXC4DIAL + 0.5 UNSAT_ALDEHYDES + 0.5 CH3CO3 + CO + HO2	8.8e-4	f
EPXC4DIAL + hν → ALD + CO + HO2	1.07e-4	f
XYL_EPOX + hν → 0.5 EPXC4MDIAL + 0.5 UNSAT_ALDEHYDES + 0.5 CH3CO3 + CO + HO2	8.8e-4	f
EPXC4MDIAL + hν → ALD + CO + HO2	1.07e-4	f

a. Maximum (noon) photolysis rate calculated following Saunders et al. (2003) for June 21, Atlanta, GA (SZA = 13.5) listed. Sinusoidal dependence on time of day assumed.
b. L = Low-NOx scheme only, H = high-NOx scheme only
c. Products from Lim et al. (2005)
d. Rate for acetaldehyde
e. Assuming fast decomposition of peroxy radical intermediate
f. Condensed from the Master Chemical Mechanism (MCM)

Table S5. Aqueous-phase photolysis reactions

Reaction	Rate[a] (s^{-1})	Reference
H2O2 + hν → 2 OH	3.77e-6	(*6*,*19*)

a. Maximum (noon) photolysis rate from reference is listed. Sinusoidal dependence on time of day assumed.

Table S6. Aqueous-phase equilibrium reactions

Reaction	k_a (M^{1-n} s^{-1})	k_r (M^{1-n} s^{-1})	Ref.
HO2 ↔ H+ + O2-	8e5	5e10	(*6*,*23*)
GLYAC ↔ GLYAC- + H+	6.94e6	2e10	(*8*)
OXLAC ↔ OXLAC- + H+	2.835e9	5e10	(*8*)
OXLAC- ↔ OXLAC-- + H+	2.71e6	5e10	(*8*)
H2SO4 ↔ bisulfate + H+	5e13	5e10	(*8*)
bisulfate ↔ sulfate + H+	1.02e9	1e11	(*8*)
FORMIC ↔ FORMIC- + H+	8.85e6	5e10	(*6*,*23*)
GLYCAC ↔ GLYCAC- + H+	6.94e6	2e10	(*6*)
ACETIC ↔ ACETIC- + H+	8.75e5	5e10	(*8*)
PYRAC ↔ PYRAC- + H+	6.4e7	2e10	(*6*)
CO2 + H2O ↔ H+ + HCO3-	5.6e4	0.024	(*6*,*17*)
HCO3- ↔ H+ + CO3-2	5e10	2.345	(*8*)

Table S7. Gas-phase thermal reactions

Reaction	Rate ((molec cm^{-3})$^{1-n}$ s^{-1})	Ref.	Note[a]
O1D + N2 → O3P + N2	1.8e-11*exp(100/T)	(*6*,*24*)	
O1D + O2 → O3P + O2	3.2e-11*exp(70/T)	(*6*,*24*)	
O3P + O2 + M → O3 + M	6e-34*(T/300)^(-2.3)	(*6*,*24*)	
O1D + H2O → 2OH	2.2e-10	(*6*,*24*)	
O3 + OH → HO2 + O2	1.6e-12*exp(-940/T)	(*6*,*24*)	
O3 + HO2 → OH + 2O2	1.1e-14*exp(-500/T)	(*6*,*24*)	
NO + OH (+M) → HONO(+M)	7.6e-12	(*6*,*24*)	
O3 + NO → NO2 + O2	2e-12*exp(-1400/T)	(*6*,*24*)	
O3 + NO2 → NO3 + O2	1.2e-13*exp(-2450/T)	(*6*,*24*)	
NO + NO3 → 2 NO2	1.5e-11*exp(170/T)	(*6*,*24*)	
NO2 + NO3 (+M) → N2O5(+M)	1.3e-12	(*6*,*24*)	
N2O5(+M) → NO2 + NO3 (+M)	6.8e-2*exp(-11080/T)	(*6*,*23*)	
NO2 + OH (+M)→ HNO3(+M)	9.7e-12	(*6*,*24*)	
NO2 + HO2 (+M) → HNO4(+M)	1.5e-12	(*6*,*24*)	
HNO4 (+M)→ NO2 + HO2(+M)	7.7e-12*exp(-10420/T)	(*6*,*23*)	
CO + OH → CO2 + HO2	1.5e-13	(*6*,*25*)	
HO2 + HO2 → H2O2 + O2	2.3e-13*exp(600/T) + 1.7e-33*2.46e19*298.15/T*exp(1000/T)	(*6*,*25*)	
H2O2 + OH → HO2 + H2O	2.9e-12*exp(-160/T)	(*6*,*24*)	
HO2 + NO → NO2 + OH	3.5e-12*exp(250/T)	(*25*)	
HO2 + OH → H2O + O2	4.8e-11*exp(250/T)	(*6*,*24*)	
SO2 + OH → SO3 + HO2	4.8e-13	(*6*,*24*)	
ISOP + OH → ISOPOO	2.7e-11*exp(390/T)	(*26*,*27*)	

ISOPOOH + OH → IEPOX + OH	1.9e-11*exp(390/T)	(*26*)	L
ISOPOOH + OH → 0.7 ISOPOO + 0.3 HC5 + 0.3 OH	0.38e-11*exp(200/T)	(*26*)	L
IEPOX + OH → IEPOXOO	5.78e-11*exp(-400/T)	(*26*)	L
FORM + OH → HO2 + CO + H2O	1.20e-14*T*exp(287/T)	(*25*)	
FORMIC + OH → HO2 + CO2 + H2O	4.5e-13	(*25*)	
GLYX + OH → HO2 + 2CO + H2O	11.4e-12	(*25*)	
MGLY + OH → CH3CO3 + CO + H2O	17.2e-12	(*25*)	
MACR + OH → 0.47 MACP + 0.53 CH3CO3	2.95e-11	(*26*)	
MVK + OH → MVKP	1.75e-11	(*26*)	
GLYC + OH → 0.71 FORM + 0.16 FORMIC + 0.35 CO2 + 0.52 CO + 0.13 GLYX + 0.75 HO2 + 0.25 OH	0.8e-11	(*26*)	
HAC + OH → 0.75 MGLY + 0.825 HO2 + 0.125 FORMIC + 0.1 OH + 0.125 CH3OO + 0.20 CO2 + 0.05 CO + 0.125 ACETIC	0.6e-11	(*26*)	
HC5 + OH → HC5OO	11e-11	(*26*)	
GLYC + OH → GLYX + HO2	2.5e-12	(*28*)	
C2H2 + OH → GLYX + OH	8.8e-13*0.636	(*29*)	
C2H2 + OH → FORMIC + CO + HO2	8.8e-13*0.364	(*29*)	
CH4 + OH → CH3OO + H2O	2.45e-12*exp(-1775/T)	(*6*,*24*)	
ALD + OH → CH3CO3 + H2O	6.87e-12*exp(256/T)	(*6*,*30*)}	
CH3OH + OH → FORM + HO2 + H2O	6.7e-12*exp(-600/T)	(*6*,*24*)	
CH3O2H + OH → 0.3 FORM + 0.3 OH + 0.7 CH3OO + H2O	3.8e-12*exp(200/T)	(*6*,*24*)	
ACETIC, GLYCAC, GLYAC, PYRAC + OH → CH3OO	4e-13*exp(200/T)	(*6*,*24*)	
OLT + OH → OLTP	5.32e-12*exp(504/T)	(*6*,*31*)	
OP2 + OH → 0.5 HC3P + 0.5 ALD + 0.5 OH	1e-11	(*6*,*31*)	
OLI + OH → OLIP	1.07e-11*exp(549/T)	(*6*,*31*)	L
KET + OH → KETP + H2O	1.2e-11*exp(-745/T)	(*6*,*31*)	
DCB + OH → TCO3 + H2O	2.8e-11	(*6*,*31*)	L
DHMOB + OH → 1.5 CO + 0.5 HO2+ 0.5 HAC + 0.5 HC4	1e-11	(*27*)	H
MOBA + OH → MOBAOO	0.3e-11	(*27*)	H
TOL + OH → 0.20 CSL + 0.238 GLYX + 0.238 MGLY + 0.198 TOL_FURANONES + 0.106 AROMATIC_KETONES + 0.20 TOL_EPOX + 0.277 UNSAT_ALDEHYDES	1.81e-12*exp(338/T)	(*32*,*33*)	
XYL + OH → 0.937 HO2 + 0.09 AROMATIC_KETONES + 0.16 MCSL + 0.09 POLY_FXNAL_AROMATIC + 0.21 XYL_EPOX + 0.317 UNSAT_ALDEHYDES + 0.247 GLYX + 0.14 MGLY + 0.07 FURANONES	1.43e-11	(*34*)	c
CSL + OH → 0.13 GLYX + 0.13 UNSAT_ALDEHYDES + 0.93 HO2 + 0.86 POLY_FXNAL_AROMATIC + 0.68 NO2	4.65e-11	(*34*)	L, c
CSL + OH → 0.13 GLYX + 0.13 UNSAT_ALDEHYDES + 0.93 HO2 + 0.86 POLY_FXNAL_AROMATIC + 0.93 NO2 + 0.01 OP2	4.65e-11	(*34*)	H, c

MCSL + OH → 0.14 MGLY + 0.14 UNSAT_ALDEHYDES + 0.93 HO2 + 0.86 POLY_FXNAL_AROMATIC + 0.68 NO2	8e-11	(*34*)	L, c
MCSL + OH → 0.10 MGLY + 0.10 UNSAT_ALDEHYDES + 0.87 HO2 + 0.79 POLY_FXNAL_AROMATIC + 0.28 NO2 + 0.11 OP2	8e-11	(*34*)	H, c
TOL_EPOX + OH → 0.38 EPXC4DIAL + 0.31 UNSAT_ALDEHYDES + 0.070 CH3CO3 + 0.31 MGLY + 0.10 CO + 0.38 HO2 + 1.32 NO2 + 0.61 ALD	7.99e-11	(*34*)	L, c
TOL_EPOX + OH → 0.28 EPXC4DIAL + 0.31 UNSAT_ALDEHYDES + 0.05 CH3CO3 + 0.22 MGLY + 0.14 CO + 0.28 HO2 + 1.37 NO2 + 0.45 ALD + 0.01 OH + 0.19 OP2	7.99e-11	(*34*)	H, c
XYL_EPOX + OH → 0.41 EPXC4MDIAL + 0.26 UNSAT_ALDEHYDES + 0.08 CH3CO3 + 0.33 MGLY + 0.10 CO + 0.40 HO2 + 1.27 NO2 + 0.66 ALD	7.88e-11	(*34*)	L, c
XYL_EPOX + OH → 0.31 EPXC4MDIAL + 0.26 UNSAT_ALDEHYDES + 0.06 CH3CO3 + 0.25 MGLY + 0.13 CO + 0.30 HO2 + 1.29 NO2 +0.50 ALD + 0.01 OH + 0.19 OP2	7.88e-11	(*34*)	H, c
EPXC4DIAL + OH → ALD + NO2	4.32e-11	(*34*)	L, c
EPXC4DIAL + OH → ALD + 0.92 NO2 + 0.01 HO2 + 0.07 OH + 0.02 O3	4.32e-11	(*34*)	H, c
EPXC4MDIAL + OH → ALD + NO2	4.32e-11	(*34*)	L, c
EPXC4MDIAL + OH → 0.01 HO2 + ALD + 0.92NO2 + 0.07 OH + 0.02 O3	4.32e-11	(*34*)	H, c
ONIT + OH → HC3P + NO2	1.55e-11*exp(-540/T)	(*6*)	
ISOPNd + OH → ISOPNOOd	9.5e-11	(*27*)	H
ISOPNb + OH → ISOPNOOb	1.3e-11	(*27*)	H
MVKN + OH → 0.65*(FORMIC + MGLY) + 0.35*(FORM + PYRAC) + NO3	0.56e-11	(*27*)	H
MACRN + OH → 0.08*(ACETIC + FORM + NO3) + 0.07*(FORMIC + NO3 + MGLY) + 0.85*(HAC + NO2) + 0.93 CO2	5e-11	(*27*)	H
ETHLN + OH → FORM + CO2 + NO2	1e-11	(*27*)	H
ISOP + O3 → 0.55 MACR + 0.21 MVK + 0.3 O3P + 0.5 OH + 0.89 FORM + 0.11 HO2 + 0.18 CO + 0.07 OLT + 0.15 ACETIC + 0.07 FORMIC + 0.09 CH3OO + 0.01 GLYX	1.23e-14*exp(-2013/T)	(*6*,*30*)	
MACR + O3 → 0.76 MGLY + 0.23 O3P + 0.46 OH + 0.7 FORM + 0.11 FORMIC + 0.23 ACETIC	4.4e-15*exp(-2500/T)	(*6*,*30*)	
MVK + O3 → 0.76 MGLY + 0.23 O3P + 0.46 OH + 0.7 FORM + 0.11 FORMIC + 0.24 CH3OO + 0.24 CO	4e-15*exp(-2000/T)	(*6*,*30*)	
OLT + O3 → 0.53 FORM + 0.5 ALD + 0.33 CO + 0.2 FORMIC + 0.2 ACETIC + 0.23 HO2 + 0.22 CH3OO + 0.1 OH + 0.06 CH4	1.32e-14*exp(-2105/T)	(*6*,*31*)	
TOL_EPOX + O3 → EPXC4DIAL + 0.70 CH3CO3 + 0.31 MGLY + 0.57 CO + 0.13	5e-18	(*34*)	c

HO2 + 0.18 NO2			
XYL_EPOX + O3 → EPXC4MDIAL + 0.70 CH3CO3 + 0.30 MGLY + 0.57 CO + 0.13 HO2 + 0.18 NO2	5e-18	(*34*)	c
FORM + NO3 → HNO3 + HO2 + CO	5.8e-16	(*6*,*24*)	
MVK + NO3 → NO2 + CH3OO + MGLY	6e-14	(*30*)	
MACR + NO3 → 0.5 HNO3 + 0.5 NO2 + 0.8 CH3CO3 + 0.5 MGLY	1e-14	(*30*)	
ALD + NO3 → CH3CO3 + HNO3	1.4e-12*exp(-1900/T)	(*6*)	
GLYX + NO3 → HO2 + HNO3 + 2 CO	6e-13*exp(-2058/T)	(*6*)	
MGLY + NO3 → CH3CO3 + HNO3 + CO	1.4e-12*exp(-1900/T)	(*6*)	
CSL + NO3 → 0.57 GLYX + 0.57 UNSAT_ALDEHYDES + 0.1 HO2 + 0.4 POLY_FXNAL_AROMATIC + 0.49 HNO3 + 3.69 NO2 + 0.02 OP2	1.4e-11	(*34*)	L, c
CSL + NO3 → 0.57 GLYX + 0.57 UNSAT_ALDEHYDES + 0.1 HO2 + 0.40 POLY_FXNAL_AROMATIC + 0.49 HNO3 + 5.03 NO2 + 0.03 OP2	1.4e-11	(*34*)	H, c
MCSL + NO3 → 0.57 MGLY + 0.57 UNSAT_ALDEHYDES + 0.1 HO2 + 0.40 POLY_FXNAL_AROMATIC + 0.49 HNO3 + 3.76 NO2 + 0.02 OP2	3.48e-11	(*34*)	L, c
MCSL + NO3 → 0.42 MGLY + 0.42 UNSAT_ALDEHYDES + 0.07 HO2 + 0.12 POLY_FXNAL_AROMATIC + 0.49 HNO3 + 1.58 NO2+0.46 OP2	3.48e-11	(*34*)	H, c
TOL_EPOX + NO3 → UNSAT_ALDEHYDES + HNO3 + 0.10 CO + 2.05 NO2	2.7254e-15	(*34*)	L, c
TOL_EPOX + NO3 → UNSAT_ALDEHYDES + HNO3 + 0.28 CO + 2.81 NO2 + 0.04 OH	2.7254e-15	(*34*)	H, c
EPXC4DIAL + NO3 → ALD + HNO3 + NO2	2.18e-14	(*34*)	L, c
EPXC4DIAL + NO3 → ALD + HNO3 + 0.92 NO2 + 0.07 OH + 0.02 O3	2.18e-14	(*34*)	H, c
XYL_EPOX + NO3 → UNSAT_ALDEHYDES + HNO3 + 0.1 CO + 2.05 NO2	1.16e-14	(*34*)	L, c
XYL_EPOX + NO3 → UNSAT_ALDEHYDES + HNO3 + 0.28 CO + 2.82 NO2 + 0.04 OH + 0.01 O3	1.16e-14	(*34*)	H, c
EPXC4MDIAL + NO3 → ALD + HNO3 + NO2	4.63e-14	(*34*)	L, c
EPXC4MDIAL + NO3 → ALD + HNO3 + 0.92NO2 + 0.07 OH + 0.02 O3	4.63e-14	(*34*)	H, c
CH3OO + HO2 → CH3O2H + O2	3.8e-13*exp(800/T)	(*6*,*24*)	
ISOPOO + HO2 → 0.880 ISOPOOH + 0.120 OH + 0.047 MACR + 0.073 MVK + 0.120 HO2 + 0.120 FORM	0.074e-11*exp(700/T)	(*26*)	L
IEPOXOO + HO2 → 0.725 HAC + 0.275 GLYC + 0.275 GLYX + 0.275 MGLY + 1.125 OH + 0.825 HO2 + 0.200 CO2 + 0.375 FORM + 0.074 FORMIC + 0.251 CO	0.074e-11*exp(700/T)	(*26*)	L

All other peroxyradicals + HO2 → OP2	7.7e-14*exp(1300/T)	(*6*,*30*)	
CH3OO + NO (+O2) → FORM + HO2 + NO2	3e-12*exp(280/T)	(*6*,*24*)	
DIBOO + NO → NO2 + HO2 + 0.52*(GLYC + MGLY) + 0.48*(GLYX + HAC)	0.81e-11	(*27*)	H
MVKP + NO → 0.625*(GLYC + CH3CO3) + 0.265*(MGLY + FORM + HO2)+ 0.11 MVKN +0.89 NO2	0.81e-11	(*27*)	
MACP + NO → 0.85*(NO2 + HO2) + 0.425*(HAC + CO) + 0.425*(FORM + MGLY) + 0.15 MACRN	0.81e-11	(*27*)	
TCO3 + NO → 0.89 GLY + 0.11 MGLY + 0.05 CH3CO3 + 0.95 CO + 2 XO2 + NO2 + 0.92 HO2	4.2e-12*exp(180/T)	(*6*,*31*)	
OLTP + NO → ALD + FORM + NO2 + HO2	4.2e-12*exp(180/T)	(*6*)	
HC3P + NO → 0.75 ALD + 0.25 KET + 0.09 FORM + 0.036 ONIT + 0.964 NO2 + 0.964 HO2	4.2e-12*exp(180/T)	(*6*)	
KETP + NO → MGLY + NO2 + HO2	4.2e-12*exp(180/T)	(*6*)	
ETHP + NO → ALD + HO2 + NO2	4.2e-12*exp(180/T)	(*6*)	
CH3CO3 + NO → NO2 + CO + CO2 + FORM + CH3OO	2.1e-11	(*27*)	
MOBAOO + NO → HC4 + CO2 + HO2 + NO2	0.8e-11	(*27*)	H
ISOPNOOb + NO → 0.6*(GLYC + HAC)+0.4*(FORM + HO2)+0.26 MACRN + 0.14 MVKN + 1.6 NO2	0.81e-11	(*27*)	H
ISOPNOOd + NO → 0.34 DHBN + 0.15 PROPNN + 0.44 HAC + 0.07 MVKN + 0.13 ETHLN + 0.31 FORMIC + 0.31 NO3 + 0.72 FORM + 0.15 GLYC + 1.34 NO2 + 0.35 HO2	0.81e-11	(*27*)	H
ISOPOO + NO → 0.26 MACR + 0.40 MVK + 0.883 NO2 + 0.66 FORM +0.07 ISOPNd + 0.047 ISOPNb + 0.10 HC5 + 0.043 MF + 0.08 DIBOO + 0.803 HO2	0.81e-11	(*27*)	H
HC5OO + NO → NO2 + 0.234*(GLYC + MGLY) + 0.216*(GLYX + HAC) + 0.29 DHMOB + 0.17 MOBA + 0.09 HC4 + 0.09 CO + HO2	0.81e-11	(*27*)	H
MVKP or MACP + ISOPOO → 0.3 MACR + 0.3 MVK + 0.6 MGLY + FORM + 1.2 HO2 + 0.1 DCB + 0.4 OLT + 0.3 OLI	3.5e-15	(*6*,*26*,*30*)	L, b
ISOPOO + ISOPOO → 0.34 MACR + 0.42 MVK + 0.3 OLT + 0.06 DCB + 0.1 OLI + 1.3 HO2 + 0.55 FORM + 0.1 MGLY	7e-16	(*6*,*26*,*30*)	L, b
CH3CO3 + NO2 → PAN	2.8e-12*exp(181/T)	(*6*,*31*)	
PAN → CH3CO3 + NO2	1.95e16*exp(-13543/T)	(*6*,*31*)	
PAN + OH → FORM + NO2 + CO	3e-14	(*35*)	
HC5OO, MOBAOO, TCO3 + NO2 → APN	1e-11	(*36*)	
APN → HC5OO, MOBAOO, TCO3 + NO2	4.6e-4	(*36*)	
APN + OH → ALD + NO2 + CO	3.2e-11	(*36*)	

a. L = Low-NOx scheme only, H = high-NOx scheme only
b. Rate adjusted to improve agreement with Paulot et al. (2009) gas-phase chamber data
c. Condensed from The Master Chemical Mechanism (MCMv3.2) (*34*,*35*)

Table S8. Aqueous-phase thermal reactions

Reaction	Rate (M^{1-n} s^{-1})	Ref.	Note[a]
OH + H2O2 → HO2 + H2O	2.7e7	(*6*,*23*)	
HO2 + H2O2 → OH + H2O + O2	3.7	(*37*)	
HO2 + HO2 → H2O2 + O2	8.3e5	(*6*,*23*,*37*)	
OH + HO2 → H2O + O2	7.1e9	(*6*,*23*)	
SO4- + SO4- → S2O8-	6.1e8	(*8*,*38*)	
SO4- + H2O2 → sulfate + H+ + HO2	1.7e7	(*8*)	CAPRAM average value
SO4- + HO2 → sulfate + H+ + O2	3.5e9	(*8*,*39*)	
SO4- + O2- → sulfate + O2	3.5e9	(*8*)	
bisulfate + OH → SO4- + H2O	3.5e5	(*8*,*40*)	
HO2 + O2- →H2O2 + O2	9.7e7	(*8*,*41*)	
OH + OH → H2O2	5.5e9	(*23*)	
OH + O2- → OH- + O2	1.0e10	(*23*)	
H2SO4 + OH → HSO4rad + H2O	1.4e7	(*39*,*42*)	
CO2- + O2 → O2- + CO2	2.4e9	(*37*)	
HCO3- + OH → H2O + CO3-	1e7	(*6*,*23*,*43*,*44*)	
CO3- + O2- → O2 + CO3-2	6.5e8	(*6*,*23*,*41*,*43*)	
CO3- + H2O2 → HCO3- + HO2	8e5	(*37*)	
CO3- + FORMIC- → HCO3- + CO2-	1.5e5	(*6*,*23*,*43*)	
GLYX + OH → GLYR + H2O	1.1e9	(*6*,*37*,*44*)	
FORMIC + OH (+O2) → COOH + H2O	1e8	(*37*,*42*)	
MGLY + OH → 0.92 PYRAC- + 0.08 GLYAC- + HO2 + H2O	7e8	(*6*,*45*)	
GLYC + OH (+O2) → GLYCR1 + H2O	5e8	(*42*,*46*)	
GLYC + OH (+O2) → GLYCR2 + H2O	1e9	(*42*,*46*)	
FORMIC- + OH (+O2) → H2O + CO2-	3.1e9*exp(-1240/T)	(*6*,*44*)	
OXLAC + OH → COOH + CO2 + 2H2O	1.4e6	(*37*,*42*)	
OXLAC- + OH → COOH + CO2- + 2H2O	2e7	(*6*,*37*,*46*)	
OXLAC-- + OH → COOH + CO2- + OH-	4e7	(*6*,*37*,*46*)	
GLYAC + OH → GLYACR + H2O	3.62e8	(*6*,*37*,*45*)	
GLYAC- + OH → GLYACR- + H2O	2.9e9	(*6*,*37*,*46*)	
GLYCAC + OH (+O2) → GLYCACR + H2O	6e8	(*42*,*47*)	
GLYCAC- + OH (+O2) → GLYCACR- + H2O	8.6e8	(*6*,*46*)	
PYRAC + OH → ACETIC + HO2 + CO2	6e7	(*6*,*45*)	
PYRAC- + OH → ACETIC- + HO2 + CO2	6e7	(*6*,*45*)	
ACETIC + OH → 0.85 GLYAC + 0.15 FORM	1.6e7	(*6*,*48*)	
ACETIC- + OH → 0.85 GLYAC- + 0.15 FORM	8.5e7	(*6*,*48*)	
ISOP + OH → 0.241 MVK + 0.109 MACR + 0.114 MGLY + 0.038 GLYX + 0.262 OXALIC + (oligomers)	1.2e10	(*49*)	
c2rad (GLYR+GLYACR+GLYACR-+GLYCR1+GLYCR2+GLYCACR+GLYCACR-) + c2rad → SUCCINIC	1.3e9	(*42*,*50*)	
c1rad (CHOHOH+COOH+CH2OH) + c2rad → MALONIC	1.3e9	(*42*,*50*)	
GLYCR1 + O2 → GLYCR1O2	1e6	(*42*,*50*)	
GLYCR2 + O2 → GLYCR2O2	1e6	(*42*,*50*)	
GLYCR1O2 → GLYCAC + HO2	50	(*42*,*51*)	
GLYCR2O2 → GLY + HO2	50	(*42*,*51*)	

GLYCR1O2 + GLYCR1O2 → CH2OH + CO2	3e8	(*42*)	
MALONIC + OH → MArad + H2O	3e8	(*42*,*52*)	
MArad + O2 → MAradO2	1e6	(*42*,*50*)	
MAradO2 → X + HO2	50	(*42*,*51*)	
MAradO2 + MAradO2 → 2 COOH + 2 GLYAC	3e8	(*42*)	
SUCCINIC + OH → SArad + H2O	1.1e8	(*42*,*52*)	
SArad + O2 → SAradO2	1e6	(*42*,*50*)	
SAradO2 → Y + HO2	50	(*42*,*51*)	
SAradO2 + SAradO2 → 2 GLYAC	3e8	(*42*)	
CHOHOH + COOH → GLYAC	1.3e9	(*42*,*50*)	
COOH + COOH → OXLAC	1.3e9	(*42*,*50*)	
GLYCR2O2 + GLYCR2O2 → GLY + GLYAC + FORMIC + CHOHOH	3e8	(*42*)	
GLYCACR + O2 → GLYCACRO2	1e6	(*42*,*50*)	
GLYR + O2 → GLYRO2	1e6	(*42*,*50*)	
GLYRO2 → GLYAC + HO2	50	(*42*,*51*)	
GLYRO2 + GLYRO2 → 2CHOHOH + 2 CO2 + O2 + 2 H2O	3e8	(*42*)	
CHOHOH + O2 → FORMIC + HO2	5e6	(*42*,*51*)	
GLYCACRO2 → GLYAC + HO2	50	(*42*,*51*)	
CH2OH + O2 → CO + HO2	1e6	(*42*,*51*)	
CHOHOH + CHOHOH → GLYX	1.3e9	(*42*,*50*)	
GLYACR + O2 → GLYACRO2	1e6	(*42*,*50*)	
GLYACRO2 → OXLAC + HO2	50	(*42*,*51*)	
GLYACRO2 + GLYACRO2 → 2 CO2 + 2 COOH	3e8	(*42*)	
COOH + O2 → CO2 + HO2	5e6	(*42*,*50*)	
GLYACR- + O2 → GLYACRO2-	1e6	(*42*,*50*)	
GLYACRO2- → OXLAC- + HO2	50	(*42*,*51*)	
GLYACRO2- + GLYACRO2- → 2 CO2- + 2 COOH	3e8	(*42*)	
FORM + SO4- → HO2 + CO + bisulfate	1.4e7	(*53*)	
FORMIC +SO4- (+O2) → bisulfate + COOH	1.4e6	(*6*,*23*,*54*)	
FORMIC- +SO4- (+O2) → bisulfate + CO2-	1.1e8	(*6*,*23*,*54*)	
GLYX + SO4- → GLYR + bisulfate	2.4e7	(*53*)	
GLYAC + SO4- → GLYACR + bisulfate	7.9e6		c
GLYACR + SO4- → GLYACOS	1e8	(*42*)	b
GLYAC- + SO4- → GLYACR- + bisulfate	6.3e7		c
GLYACR- + SO4- → GLYACOS	1e8	(*42*)	b
GLYR + SO4- → GLYOS	1e8	(*42*)	b
GLYCR1 + SO4- → GLYCOS	1e8	(*42*)	b
GLYCR2 + SO4- → GLYCOS	1e8	(*42*)	b
GLYCACR + SO4- → GLYCACOS	1e8	(*42*)	b
GLYCACR- + SO4- → GLYCACOS	1e8	(*42*)	b
ISOP + SO4- → ISOPOS	1e8	(*42*,*55*)	d
MVK + SO4- → MVKOS	1e8	(*42*,*55*)	d
MACR+ SO4- → MACROS	1e8	(*42*,*55*)	d
GLYR + HSO4rad → GLYOS	1e8	(*42*)	
GLYCR1 + HSO4rad → GLYCOS	1e8	(*42*)	
GLYCR2 + HSO4rad → GLYCOS	1e8	(*42*)	
GLYCACR + HSO4rad → GLYCACOS	1e8	(*42*)	
GLYCACR- + HSO4rad → GLYCACOS	1e8	(*42*)	

IEPOX + sulfate → IEPOXOS	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * BETA	(*60*)	L, e
IEPOX + H2O → tetrol	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * (1-BETA)	(*60*)	L, e
TOL_EPOX + sulfate → TOL_EPOX OS	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * BETA	(*60*)	f
TOL_EPOX + H2O → TOL_EPOX diol	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * (1-BETA)	(*60*)	f
EPXC4DIAL + sulfate → EPXC4DIALOS	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * BETA	(*60*)	f
EPXC4DIAL + H2O → EPXC4DIAL_diol	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * (1-BETA)	(*60*)	f
XYL_EPOX + sulfate → XYL_EPOX OS	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * BETA	(*60*)	f
XYL_EPOX + H2O → XYL_EPOX diol	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * (1-BETA)	(*60*)	f
EPXC4MDIAL + sulfate → EPXC4DIAL OS	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * BETA	(*60*)	f
EPXC4MDIAL + H2O → EPXC4DIAL_diol	(5e-2*aH +2e-4 *[sulfate]*aH +7.3e-4*[bisulfate]) * (1-BETA)	(*60*)	f

a. L = Low-NOx scheme only, H = high-NOx scheme only
b. Assume same mechanism, rate as HSO4rad
c. Assume the same ratio as glyoxal for the rates of H abstraction by SO4- vs. OH
d. Mechanism from Nozière et al. (2010), assuming rate following Perri et al. (2010)
e. aH = activity of H+. BETA = Branching ratio, assumed to be 0.4 based on highest sulfate concentration studied by Eddingsaas et al. (2010)
f. Assuming same mechanism, rate as IEPOX

Table S9. Model Initial Conditions. For all gas-phase species not listed here, initial concentration = 0. Values adopted from CAPRAM 3.0 (*8*) except as noted.

Species	Low-NOx (ppb)	High-NOx (ppb)	Note
Isoprene	1	0.1	
Glyoxal	0.1	0.1	
Methylglyoxal	0.1	0.1	
CO	150	200	
HOOH	1	1	
OH	4e-5	4e-5	estimate
Formaldehyde	0.5	0.1	
Acetic acid	0.001	0.001	
SO2	1	10	
NO2	0.3	4.5	
HNO3	0.3	1	
O3	40	90	
C2H2	0.5	3	(*57*)
OLT	0.1	0.1	
ALD	0.1	0.1	
OP2	0.01	0.01	
KET	0.1	0.1	
CH3OH	2	5	
CH3O2H	0.01	0.01	
PAN	0.01	0.01	
APN	0.001	0.001	Estimate
Toluene	0.01	0.1	
Cresol	0.001	0.001	
Xylenes	0.01	0.1	
CO2	3.57e5	5e5	
CH4	1700	1700	
H2O	Calculated based on specified RH		

Table S10. Emissions. All values adopted from CAPRAM 3.0 (*8*). Assumes mixing height of 10^5 cm.

Species	Low-NOx (cm^{-2} s^{-1})	High-NOx (cm^{-2} s^{-1})	Note
Isoprene	1.5e6	1.54e5	= 0 at nighttime
CO	3.7e6	8.99e7	
Formaldehyde	3028	2.58e5	
Acetic acid	3350	8.44e4	
SO2	2.91e5	3.27e7	
NO	2.86e5	1.01e7	
OLT	7950	4.94e5	
ALD	3171	5.93e5	
KET	8920	9.9e5	
CH3OH	1.07e4	1.16e6	
CH3OOH	3350	8.44e4	Assumed same as acetic acid
Toluene	2.108e4	1.7e6	
Cresol	2.88e4	1.82e6	
Xylenes	1.13e4	9.88e5	

Table S11. Deposition rates. All values adopted from CAPRAM 3.0 (*8*). Assumes mixing height of 10^5 cm.

Species	Deposition rate (s^{-1})
CO	1e-6
HOOH	1e-5
Formaldehyde	1e-5
Formic acid	1e-5
SO2	1e-5
NO2	4e-6
N2O5	2e-5
HNO3	2e-5
O3	4e-6
CH3OH	1e-5
CH3O2H	5e-6

Table S12. List of SOA molecular weights, O:C ratios, and H:C ratios

Species Name	Abbreviation	Formula	Molecular Weight	O:C	H:C
2-methyl tetrol	[tetrol]	C5H12O4	136.15	0.8	2.4
Formic acid	[FORMIC]	CH2O2	46.03	2	2
Formate ion	[FORMIC-]	CHO2	45.02	2	1
Glycolic acid	[GLYCAC]	C2H4O3	76.05	1.5	2
Glycolate (I) ion	[GLYCAC-]	C2H3O3	75.04	1.5	1.5
Pyruvic acid	[PYRAC]	C3H4O3	88.06	1	1.33
Pyruvate (I) ion	[PYRAC-]	C3H3O3	87.05	1	1
Acetic acid	[CH3CO2H]	C2H4O2	60.05	1	2
Acetate ion	[CH3CO2-]	C2H3O2	59.04	1	1.5
Carbon dioxide	[CO2]	CO2	44.01	2	0
Isoprene	[ISOP]	C5H8	68.12	0	1.6
Glyoxal-derived organosulfate	[GLYOS]	C2H2O6S	122.03	3	1
Glycolaldehyde-derived organosulfate	[GLYCOS]	C2H4O6S	124.05	3	2
Glyoxylic acid-derived organosulfate	[GLYCACOS]	C2H4O7S	140.05	3.5	2
Succinic acid	[SUCCINIC]	C4H6O4	118.09	1	1.5
Malonic acid	[MALONIC]	C3H4O4	104.06	1.33	1.33
Carbon monoxide	[CO]	CO	28.01	1	0
Carbon dioxide anion	[CO2-]	CO2-	44.01	2	0
Bicarbonate (I) ion	[HCO3-]	HCO3-	61.02	3	1
Carbonate (II) ion	[CO3--]	CO3--	60.01	3	0
Carbonate radical	[CO3-]	CO3--	60.01	3	0
2,3-epoxy-6-oxo-heptanal	TOL_EPOX	C7H6O3	138.06	0.43	0.86
2,3-epoxy-6-oxo-heptanal derived diols	TOL_EPOX diol	C7H8O4	156.08	0.57	1.14

2,3-epoxy-6-oxo-heptanal derived organosulfates	TOL_EPOX OS	C7H8O7S	239.08	1	1.14
Unsaturated aldehydes[a]	ALD	n/a	97.4	0.43	1.27
C4-epoxy-dial	EPXC4DIAL	C4H4O3	100.04	0.75	1
C4-epoxy-dial-derived diols	EPXC4DIAL diol	C4H6O4	118.06	1	1.5
C4-epoxy-dial-derived organosulfates	EPXC4DIAL OS	C4H6O7S	201.06	1.75	1.5
Xylene-derived epoxide	XYL_EPOX	C8H10O3	154.1	0.38	1.25
Xylene-derived epoxide diols	XYL_EPOX_DIOL	C8H12O4	172.12	0.5	1.5
Xylene-derived epoxide organosulfates	XYL_EPOX_OS	C8H12O7S	255.12	0.88	1.5
Methyl-C4-epoxy-dial	EPX4MDIAL	C5H6O3	114.06	0.6	1.2
Methyl-C4-epoxy-dial diols	EPX4MDIAL_DIOL	C5H8O4	132.08	0.8	1.6
Methyl-C4-epoxy-dial organosulfate	EPX4MDIAL_OS	C5H8O7S	215.08	1.4	1.6

a. Average of values considered.

II. Density functional theory calculations

Ab initio calculations were used to analyze the reaction pathways for the hydrolysis and reaction with HSO_4^- for TOL_EPOX, XYL_EPOX, EPXC4DIAL, and EPXMC4DIAL. Geometry optimizations, transition state searches, and energy calculations were performed using Jaguar 7.0 (Schrödinger). Density functional theory (DFT) with the B3LYP functional and 6-31G** basis set was used. These ab initio calculations were performed for gas phase species. Including Poisson-Boltzmann solvation with a water solvent did not significantly impact the calculation results (*58,59*).

Rate constants were calculated from the output of the Jaguar calculations using transition state theory as follows:

$$k = L^{\ddagger} \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} \exp\left(-\frac{\Delta E_0}{k_B T}\right) \qquad \text{(S1)}$$

where $L^{\ddagger}$ is a symmetry correction factor, k_B is Boltzman's constant, T is absolute temperature, h is Planck's constant, and ΔE_0 is the change in zero point energy. Q_A, Q_B, and $Q^{\ddagger}$ are the overall partition functions for the reactants and the transition state.

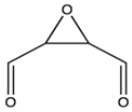
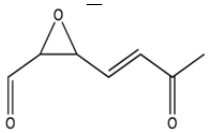
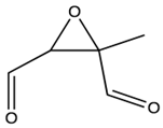
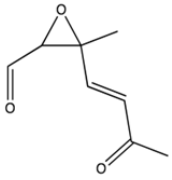
Our results show that hydrolysis and organosulfate formation are thermodynamically favorable for each of the epoxide precursors studied. Changes in Gibbs free energy for the reactions are summarized in Table S12. All of the reactions are exothermic. The rate determining step for each reactive system was found to be the attack of the nucleophile (HSO_4^- or H_2O) on the protonated epoxide. Note that the ΔG values reported for the hydrolysis reactions in Table S12 do not take into account deprotonation of the hydrolysis product after H_2O addition. This step was found to be endothermic, with ΔG ranging from +22 to +33 kcal mol^{-1}, in our gas-

phase calculations. Despite the endothermic nature of this step, the overall ΔG including deprotonation is still negative for each of the hydrolysis pathways studied. The deprotonation step would likely be facilitated in an aqueous environment as compared to our gas-phase calculations.

Using the data for the rate determining transition states, we calculated the rate constants for each reaction. These results are also summarized in Table S12. Each of the reactions are predicted to have large rate constants relative to those that have been recently measured for the IEPOX hydrolysis and organosulfate reactions (*56,60*). Significant uncertainty exists in predictions of rate constants using density functional theory, so for the purposes of GAMMA we have assumed that each of these reactions proceeded at the observed rates for IEPOX.

Taken together, our calculations predict that the formation of SOA and organosulfates from TOL_EPOX, XYL_EPOX, EPXC4DIAL, and EPXMC4DIAL should be thermodynamically and kinetically favorable. These predictions should be confirmed experimentally, and rate constants for these processes should be measured.

Table S12. Calculated overall free energy changes and rate constants for aqueous aerosol-phase reactions of toluene and xylene-derived epoxides

Epoxide precursor	Reaction	ΔG (kcal mol^{-1})	Rate Constant k (M^{-1} s^{-1})
EPXC4DIAL 	Protonation	-5.56	
	Hydrolysis	-35.22	2.95E+04
	HSO_4^- addition	-155.99	6.43E+03
TOL_EPOX 	Protonation	-24.47	
	Hydrolysis	-29.20	1.02E+03
	HSO_4^- addition	-149.88	1.12E+01
EPXMC4DIAL 	Protonation	-7.37	
	Hydrolysis	-39.67	2.14E+03
	HSO_4^- addition	-151.88	4.03E+02
XYL_EPOX 	Protonation	-38.97	
	Hydrolysis	-42.02	5.38E+05
	HSO_4^- addition	-148.79	1.17E+01

III. Model comparison with experiments of Paulot et al. (2009a)

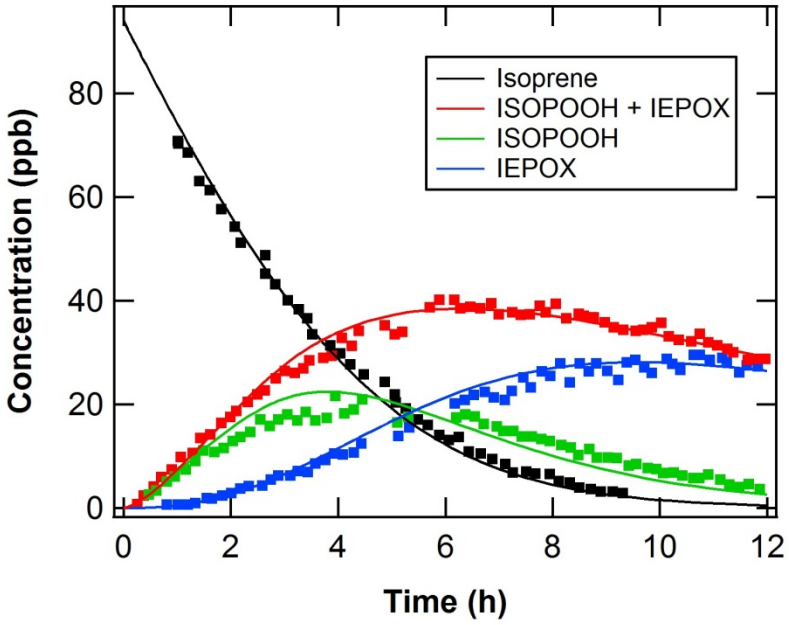


Figure S1. Comparison of low-NOx model output (curves) with experimental data from Paulot et al. (2009a) (points).

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