Supplementary material for "Global modeling of SOA formation from dicarbonyls, epoxides, organic nitrates and peroxides"

Guangxing Lin[1], Joyce E. Penner[1], Sanford Sillman[1], Domenico Taraborrelli[2], and Jos Lelieveld[2,3]

[1]Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, Ann Arbor, Michigan, USA.

[2]Department of Atmospheric Chemistry, Max Planck Institute for Chemistry, Mainz, Germany.

[3]The Cyprus Institute, Nicosia, Cyprus.

Correspondence to: Guangxing Lin (gxlin@umich.edu)

This supplementary material includes four tables. Table S1 shows SVOCs that partition to aerosol phase through gas-particle partitioning, parent VOCs, partitioning coefficients (K) at temperature 298K, oligomer formation rates for each SVOC species and its relative contribution (annual global mean) to total ne_oSOA in three different simulations. The other three tables describe the chemical species (Table S2) and reactions (Table S3 and S4) used in the HO_x recycling mechanism in Simulation B and C.

Table S1. SVOCs that partition to aerosol phase through gas-particle partitioning, parent VOCs, partitioning coefficients (K) at temperature 298K, oligomer formation rates for each SVOC species and its relative contribution (annual global mean) to total ne_oSOA in three different simulations.

Short name	Chemical formula	Parent VOC	K (m^3/μg)	Production (Tg/year)			% contribution to ne_oSOA		
				Simulation A	Simulation B	Simulation C	Simulation A	Simulation B	Simulation C
A-DI	C6H5OH(OH)CHO	aromatics	1.47E-03	8.11E-02	5.12E-02	6.32E-02	0.33	0.34	0.24
AD2P	C6H4(CH3)OH(OH)OOH	aromatics	1.01E-1	1.59E+00	1.47E+00	1.53E+00	6.47	9.71	5.74
AP	C6H5OH(OH)C(O)OOH	aromatics	8.34E-1	1.35E+00	1.26E+00	1.30E+00	5.52	8.35	4.87
APAN	C6H5OH(OH)CO3NO2	aromatics	1.76E-1	6.85E-01	6.43E-01	6.74E-01	2.80	4.26	2.53
DPAN	CHOCH=CHCO3NO2	aromatics	4.34E-07	3.79E-05	3.43E-05	3.83E-05	1.55E-04	2.27E-04	1.44E-04
GPAN	HOCH2C(O)OONO2	isoprene	6.33E-07	1.72E-03	1.05E-08	1.32E-08	7.04E-03	6.96E-08	4.94E-08
NITP	C6H5ONO2	aromatics	3.24E-07	7.76E-05	3.66E-05	5.05E-05	3.17E-04	2.42E-04	1.90E-04
XAP	CH3COCH=CHC(O)OOH	aromatics	1.12E-05	1.21E-04	7.09E-05	8.89E-05	4.93E-04	4.69E-04	3.34E-04
XPAN	CH3COCH=CHCO3NO2	aromatics	1.81E-06	4.56E-05	3.64E-05	4.20E-05	1.86E-04	2.41E-04	1.58E-04
YAP	CHOCH=C(CH3)C(O)OOH	aromatics	7.24E-06	8.54E-05	4.78E-05	6.10E-05	3.49E-04	3.16E-04	2.29E-04
YPAN	CHOCH=C(CH3)CO3NO2	aromatics	1.33E-06	3.43E-05	2.66E-05	3.10E-05	1.40E-04	1.76E-04	1.17E-04
ZAP	CHOC(CH3)=CHC(O)OOH	aromatics	7.54E-06	8.90E-05	4.97E-05	6.36E-05	3.63E-04	3.29E-04	2.39E-04
ZPAN	CHOC(CH3)=CHCO3NO2	aromatics	1.38E-06	3.56E-05	2.76E-05	3.22E-05	1.45E-04	1.83E-04	1.21E-04
IAP	HOCH2C(CH3)(OOH)CH(OH)CHO	isoprene	7.77E-02	4.58E+00	8.71E-01	2.12E+00	18.70	5.76	7.97
INPN	O2NOCH2C(OOH)(CH3)CH=CH2	Isoprene	1.83E-05	3.91E-03	2.77E-03	3.43E-03	1.60E-02	1.83E-02	1.29E-02
ISNP	HOCH2C(OOH)(CH3)CH(ONO2)CH2OH	Isoprene	3.39E+00	1.06E+00	4.51E-01	6.79E-01	4.32	2.98	2.55
LIP	HOC10H16OOH	Limonene	2.54E-02	8.10E-01	1.07E+00	1.07E+00	3.30	7.09	4.01
MRP	HOCH2C(OOH)(CH3)CHO	from MACR, isoprene, limonene, alpha pinene	6.15E-05	9.94E-03	2.00E-03	3.39E-03	4.06E-02	1.33E-02	1.27E-02
PINT	ONO2C10H16OOH	alpha pinene and limonene	1.55E-02	2.05E-01	1.11E-01	1.57E-01	0.84	0.74	0.60
PIP	HOC10H16OOH	alpha pinene	7.58E-03	7.87E-01	8.02E-01	8.63E-01	3.21	5.31	3.24
VRP	HOCH2CH(OOH)C(O)CH3	Isoprene	9.90E-05	2.01E-02	4.25E-03	7.75E-03	8.21E-02	2.81E-02	2.91E-02
DB1OOH	HOCH=C(CH3)CH(OOH)CH2OH + HOCH2C(CH3)(OOH)CH=CHOH	Isoprene	6.40E-03	-	5.22E-01	1.41E+00	-	3.45	5.30
DB2OOH	CHOC(CH3)(OOH)CHOHCH2OH + HOCH2C(CH3)(OH)CH(OOH)CH2OH	Isoprene	1.10E-01	-	2.47E+00	6.34E+00	-	16.3	23.8
TRIOL	HOCH=C(CH3)CH(OH)CH2OH + HOCH2C(CH3)(OH)CH=CHOH	isoprene	4.78E-06	-	1.67E-06	5.16E-06	-	1.10E-05	1.94E-05
PRN2	C4H7O6N	Isoprene	4.42E-02	1.34E+01	8.07E+00	1.04E+01	54.5	53.4	39.1
RIP	HOCH2C(OOH)(CH3)CH=CH2	isoprene	1.77E-05	7.04E-03	1.09E-03	3.28E-03	2.87E-02	7.21E-03	1.23E-02
Total anthropogenic sources			-	3.7	3.4	3.6	15.1	19.1	13.5
Total biogenic sources			-	20.8	14.4	23.0	84.9	80.9	86.5

Table S2. Additional species used in the HO_x recycling mechanism and in the epoxide formation mechanism

Symbol	Formula	Description
RIPEEO2	Z-HOCH2C(CH3)=CHCH2O2 + Z-CH2O2C(CH3)=CHCH2OH	Z isomers of the internally double bonded isoprene peroxy radicals
RIPEEOOH	Z-HOCH2C(CH3)=CHCH2OOH + Z-CH2OOHC(CH3)=CHCH2OH	Hydroperoxide from RIPEEO2
DB1O2	HOCH=C(CH3)CH(O2)CH2OH + HOCH2C(CH3)(O2)CH=CHOH	first-generation RO2 from Dibble mechanism (Paulot et al., 2009a)
DB2O2	CHOC(CH3)(O2)CHOHCH2OH + HOCH2C(CH3)(OH)CH(O2)CH2OH	second-generation RO2 from Dibble mechanism (Paulot et al., 2009a)
DB1OOH	HOCH=C(CH3)CH(OOH)CH2OH + HOCH2C(CH3)(OOH)CH=CHOH	Hydroperoxide from DB1O2
DB2OOH	CHOC(CH3)(OOH)CHOHCH2OH + HOCH2C(CH3)(OH)CH(OOH)CH2OH	Hydroperoxide from DB2O2
TRIOL	HOCH=C(CH3)CH(OH)CH2OH + HOCH2C(CH3)(OH)CH=CHOH	Triol from the molecular channel of DB1O2 permutation reaction
ZCO3HC23DBCOD	HOCH=C(CH3)CH(OH)CH2OH + HOCH2C(CH3)(OH)CH=CHOH	Acylhydroperoxyaldehydes (PACALD) predicted by Peeters et al., (2009)
ZCODC23DBCOOH	CHOC(CH3)=CHCH2OOH + HOOCH2C(CH3)CHCHO	Hydroperoxyaldehydes (HPALD) predicted by Peeters et al., (2009)
IEPOXO2		RO2 from isoprene epoxide
HAC	HOCH2C(O)CH3	Hydroxyacetone
GLYC	HOCH2CHO	Glyxoaldehyde
GLYX	CHOCHO	Glyoxal
MGLY	CH3COCHO	Methylglyoxal
HCHO	CH2O	Formaldehyde
ACO2	HCOOH	Formic acid

Table S3. Additional reactions for HO_x recycling mechanism

	Reaction	Rate constant	References	Notes
1	RIPEEO2 => ZCODC23DBCOOH + HO2	9.82E8 * EXP(-6303/T)	Peeters et al. (2009)	1,6-H-shift
2	RIO2 => 0.864 HO2 + 0.690 HCHO + 0.402 MVK + 0.288 MACR + 0.136 RIO1 + 0.127 IALD	6.08E10 * EXP(-8893/T)	Peeters et al. (2009)	1,5-H-shift for MVK and MACR precursors; Although the parent RO2 of IALD do not undergo 1,5-H-shift, for simplicity the products of RIO2 + NO are taken except NO2
3	RIPEEO2 + HO2 => RIPEEOOH	2.91E-13 * EXP(1300./T) * 0.706		MCM rate constant
4	RIPEEO2 + MO2 => IAP + HO2 + HCHO + HO2	K same as for IAO2 + MO2		
5	RIPEEO2 + NO => IAP + HO2 + NO2	2.54E-12 * EXP(360./T)		Rate constant as for the others first-generation RO2 from isoprene
6	RIPEEOOH + hv => OH + IAP + HO2	J(CH3OOH)		
7	RIPEEOOH + OH => 0.5 IEPOX + 0.25MGLY + 0.25GLYX + 0.25HOOCH2CHO + 0.25CH3COCH2OOH	k= same as for RIP + OH		approximation: a carbonyl function should have been an -OH functional group
8	ZCODC23DBCOOH + OH => 0.5MGLY + 0.5 HOOCH2CHO + 0.5CH3COCH2OOH + 0.5GLYX	4.50E-11	SAR (Taraborrelli et al., 2012.)	rate constant calculated by SAR by and similar to the estimate of Peeter and Mueller, PCCP 2010
9	ZCODC23DBCOOH + hv => OH + IAO2	J(CH3OOH)+J(MACR)/0.004		J value for MACR photolysis assuming IMPACT has a quantum yield of 0.004 (as recommended by IUPAC). IAO2 should represent LHC4ACCO3 of MIM2
10	CH3COCH2OOH + OH => ATO2	1.90E-12 * EXP(190/T)	IUPAC	H-abstraction channel from the –OOH group
11	CH3COCH2OOH + OH => MGLY + OH	8.39E-12	SAR	H-abstraction from

			(Taraborrelli et al., 2012.)	the –CH2OOH group with following prompt OH-elimination
12	CH3COCH2OOH + hv => MCO3 + HCHO + OH	J(MEK) + J(CH3OOH)		Structural analogy to methyl ethyl ketone and methyl hydroperoxide
13	IAO2 => ZCO3HC23DBCOD + HO2	7.32E8 * EXP(-5556./T)	Peeters et al. (2009)	1, 6-H-shift
14	ZCO3HC23DBCOD + hv => MCO3 + 2CO2 + 2OH + HO2 + CO	J(CH3OOH)+J(MACR)/0.004	Peeters et al. (2009)	enhanced photolysis
15	VRO2 => 0.7MGLY + 0.7HCHO + 0.3HOOCH2CHO + 0.3MCO3 + OH	5.1E10 * EXP(-8893/T)	Peeters et al. (2009)	1,5-H-shift
16	MRO2 => 0.830 HCHO + 0.830 MGLY1 + 0.170 + HAC + 0.170 CO + .17 HO2 + OH	4.5E10*EXP(-8893/T)	Peeters et al. (2009)	1,5-H-shift
17	HOOCH2CHO + OH => OH + 0.44HCHO + 0.44CO + 0.56GLYX	2.081E-11		0.29 HCOCH2O2 neglected and the other two yields re-scaled with a factor of 1/(1-.29)
18	HOOCH2CHO + hv => OH + HCHO + CO + HO2	J(CH3OOH)+J(GLYC)		Structural analogy to glycolaldehyde and methyl hydroperoxide
19	DB1O2 + MO2 => 0.8 DB2O2 + 0.2 TRIOL + HCHO + HO2	2.9E-12		MCM rata constant for a secondary RO2
20	DB1O2 + HO2 => DB1OOH	0.706 * 2.91E-13 * EXP(1300./T)		MCM rate constant
21	DB1O2 + NO => DB2O2 + NO2	2.54E-12 * EXP(360./T)		Rate constant as for the others first-generation RO2 from isoprene
22	DB2O2 + MO2 => 0.5 HAC + 0.5 GLYC + 0.5 MGLY + 0.5 GLYX + HO2 + HCHO + HO2	2.9E-12		MCM rata constant for a secondary RO2
23	DB2O2 + HO2 => DB2OOH	0.706 * 2.91E-13 * EXP(1300./T)		MCM Rate constants
24	DB2O2 + NO => 0.5 HAC + 0.5 GLYC + 0.5 MGLY + 0.5 GLYX + HO2 + NO2	2.54E-12 * EXP(360./T)		Rate constant as for the others first-generation RO2 from isoprene
25	DB1OOH + OH = >DB1O2	0.4*k_CH3OOH_OH		
26	DB1OOH + hv => DB2O2 + OH	J(CH3OOH)		Structural analogy to methyl hydroperoxide
27	DB2OOH + OH => DB2O2	0.4*k_CH3OOH_OH		

28	DB2OOH + hv => 0.5 HAC + 0.5 GLYC + 0.5 MGLY + 0.5 GLYX + HO2 + OH	J(CH3OOH)		Structural analogy to methyl hydroperoxide
29	TRIOL + OH => IAO2	1E-11	SAR (Taraborrelli et al., 2012.)	Triol from permutations reactions of DB1O2

Table S4. Modified reactions in HOx recycling mechanism

	Modified reactions	Original reactions	References	Notes
1	MAO3 + HO2 => 0.44 OH + 0.44 HO2 + 1.76HCHO + 0.350 MAOP + 0.150 RCOH	MAO3 + HO2 => 0.7MAOP + 0.30 RCOH + 0.3O3		Structural analogy to MCO3
2	MCO3 + HO2 => 0.44 OH + 0.44 MO2 + 0.35 MAP + .15 ACTA + .15 O3	MCO3 + HO2 => O3 + ACTA MCO3 + HO2 => MAP	IUPAC, 2009	
3	RIO2 + NO => NO2 + 0.864 HO2 + 0.690 HCHO + 0.402 MVK + 0.288 MACR + 0.09 DB1O2 + 0.046 RIO1 + 0.127 IALD	RIO2 + NO => NO2 + 0.864 HO2 + 0.690 HCHO + 0.402 MVK + 0.288 MACR + 0.136 RIO1 + 0.127 IALD	Paulot et al., (2009a)	
4	MO2 + RIO2 => 1.864 HO2 + 1.690 HCHO + 0.402 MVK + 0.288 MACR + 0.09 DB1O2 + 0.046 RIO1 + 0.127 IALD	MO2 + RIO2 => 0.25MOH + 0.92HO2 + HCHO +0.2MVK + 0.14MACR +0.07RIO1 + 0.06IALD +0.25MEK +0.25ROH	This work	Consistent with Paulot et al., (2009a)
5	MCO3 + RIO2 => MO2 + 0.864 HO2 + 0.690 HCHO + 0.402 MVK + 0.288 MACR + 0.09 DB1O2 + 0.046 RIO1 + 0.127 IALD	MCO3 + RIO2 => MO2 + 0.864HO2 + 0.690HCHO + 0.402MVK + 0.288MACR + 0.136RIO1 + 0.127IALD	This work	Consistent with Paulot et al., (2009a)
6	RIO2 + RIO2 => 1.728 HO2 + 1.38 HCHO + 0.804 MVK + 0.576 MACR + 0.18 DB1O2 + 0.092 RIO1 + 0.254 IALD	RIO2 + RIO2 => 0.680MVK + 0.390MACR + 0.930IPRD +0.40HCHO + 1.380HO2	This work	Consistent with Paulot et al., (2009a)
7	RIO2 + HO2 => RIP	RIO2 + HO2 => 0.88RIP + 0.12OH + 0.047MACR + 0.073MVK + 0.120HCHO + 0.120HO2		the 12% yield of OH was used in Paulot et al., (2009b) in order to account for the initial NOx present in the "low-NOx" experiments
8	RIO1 + HO2 => RIP	RIO1 + HO2 => 0.88RIP + 0.12OH + 0.047MACR + 0.073MVK + 0.120HCHO + 0.120HO2		The same above
9	GLYX + OH => 1.8 CO + 0.8 HO2 + 0.2 OH	GLYX + OH => HO2 +2CO	This work	Combination of results from Orlando and Tyndall, (2001), Feierabend et al.,

				(2008)
10	GLYC + OH => 0.75 HO2 + 0.25 OH + 0.13 GLYX + 0.52 CO + 0.16 HCOOH + 0.71 HCHO	GLYC + OH => 0.80GCO3 + 0.20 GLYX + 0.20HO2	Butkovskaya et al., (2006a)	
11	HAC + OH => 0.75 MGLY + 0.825 HO2 + 0.125 HCOOH + 0.1 OH +0.125 MO2 + 0.05 CO + 0.125 ACTA	HAC + OH => MGLY + HO2	Butkovskaya et al., (2006b)	
12	RIP + OH => 0.5 IAO2 + 0.50MGLY + 0.50GLYX + 0.50CH3COCH2OOH + 0.50HOOCH2CHO	RIP + OH => 0.50IAO2 + 0.4RIO2 + 0.2RIO1	This work	Approximation regarding the degradation products

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