Supplement of

Secondary organic aerosol formation from smoldering and flaming combustion of biomass: a box model parametrization based on volatility basis set

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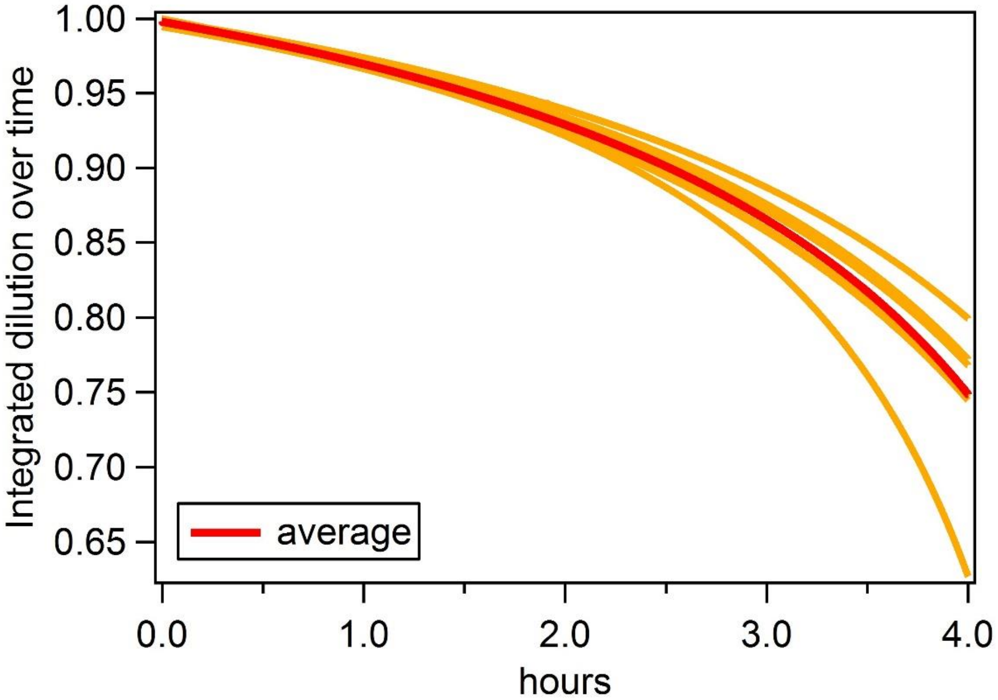

Figure S1. Integrated dilution over time calculated for each experiment in Set1 and average dilution ratio across all (Set1) experiments. The average OH exposure at the end of the experiment is 6.3 × 10^6 molec cm^{-3} h.

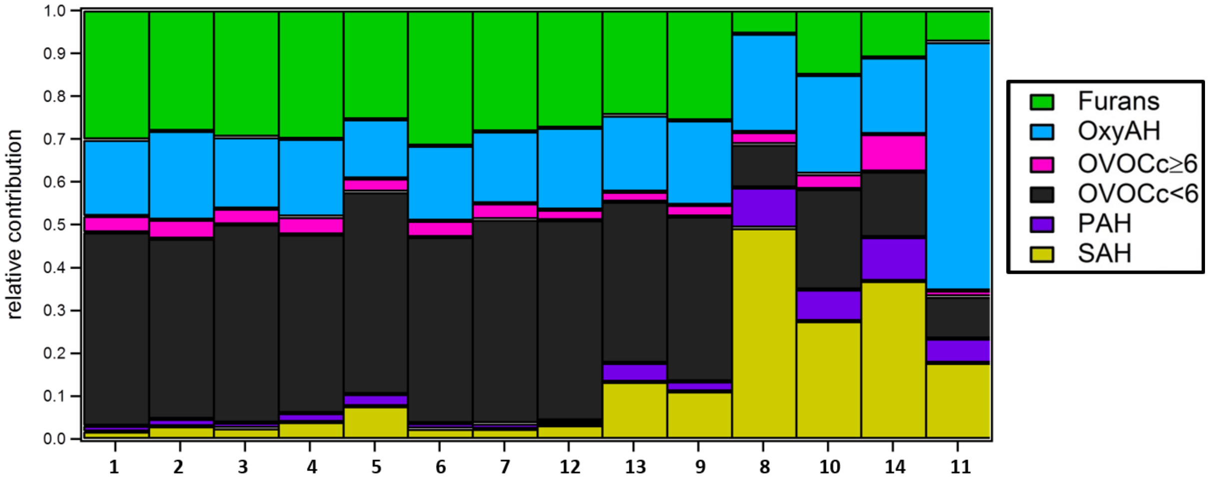

Figure S2. Relative contributions of different primary VOCs families (measured in µg m^{-3}) for each experiment. The experiments from Set2 (8-14) are ordered based on similarity with Set1 (1-7).

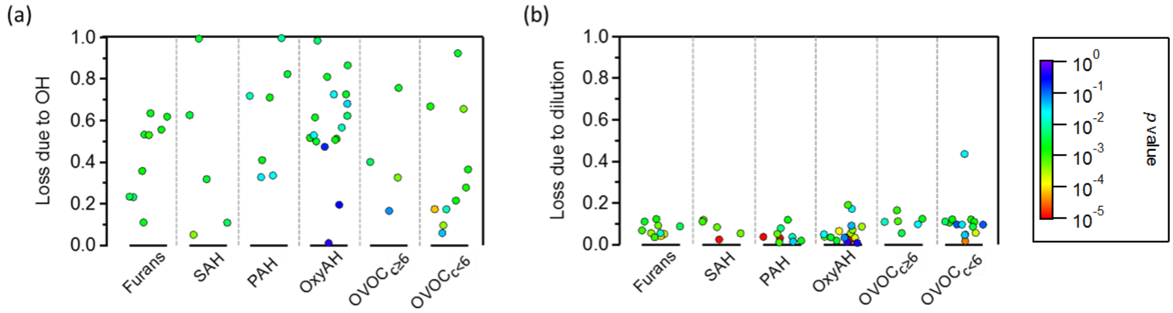

Figure S3. Fraction of consumed precursor compounds for Set2 by OH oxidation (a) and dilution (b) at the end of the experiments. Each point corresponds to a single compound averaged among experiments, accounting for its standard deviation, normalized for initial concentration. The color legend represents the statistical significant deviation from zero reactivity with the investigated reactant (*p* value).

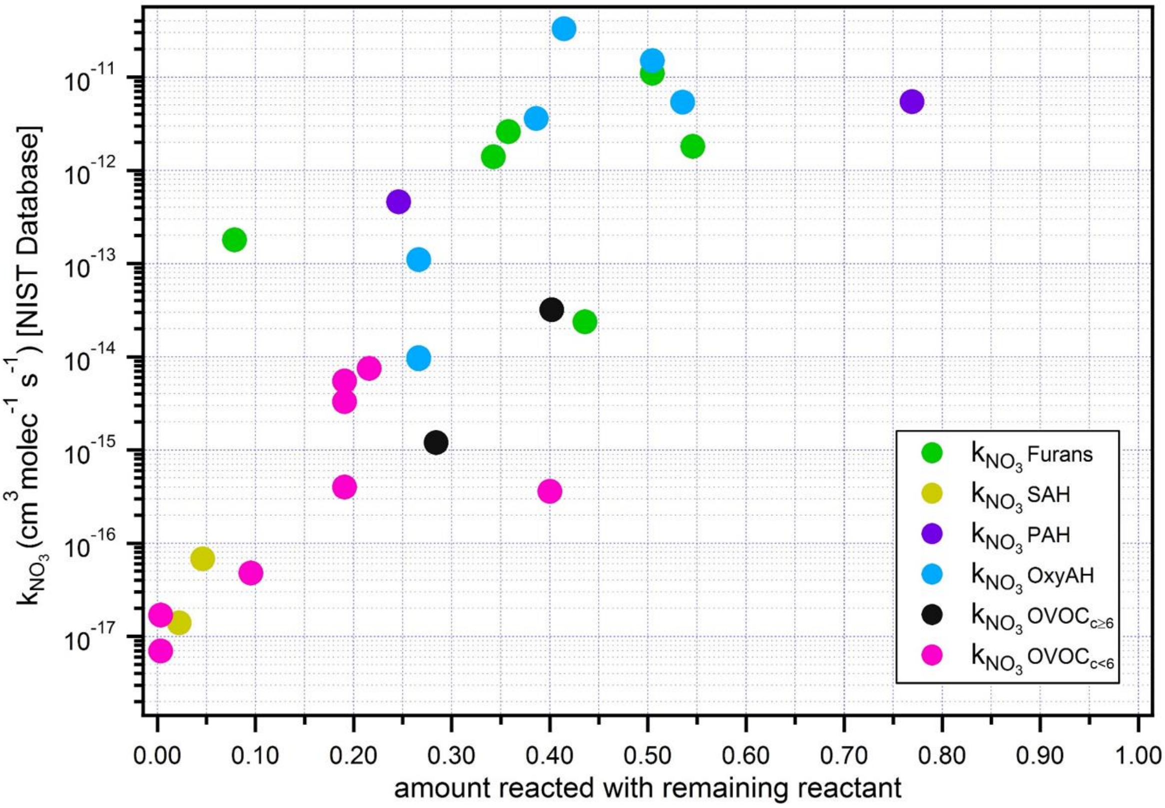

Figure S4. Reaction rates towards NO_3 from NIST database (NIST Chemistry WebBook, 2018) versus amount reacted with the remaining oxidant for different compounds. All data is from Set1 experiments.

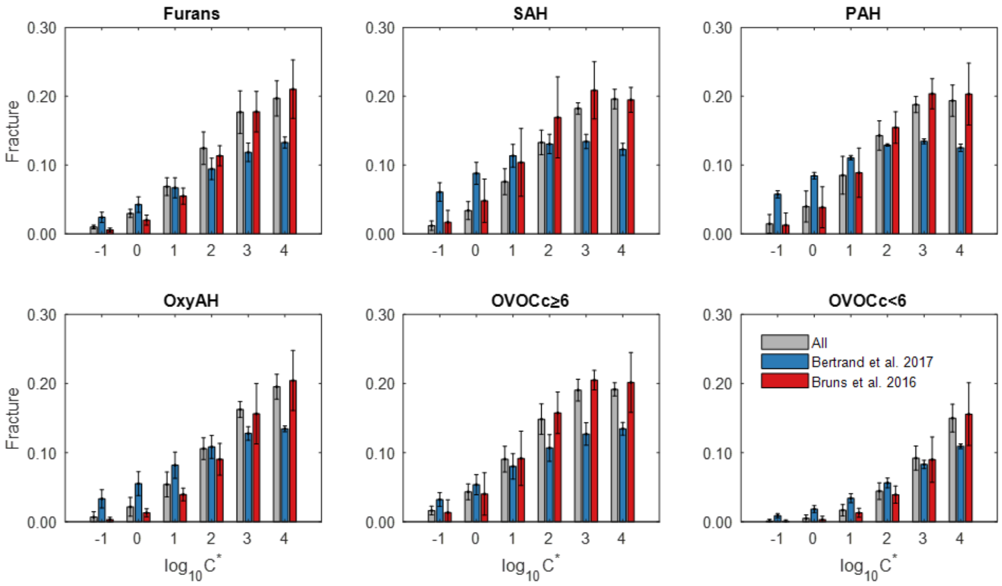

Figure S5. Volatility distributions of different precursor classes for Bertrand et al. (2017) (Set1) and Bruns et al. (2016) (Set2), and both of them (labelled "all"). The error bars represent the standard error of 30 bootstrap runs.

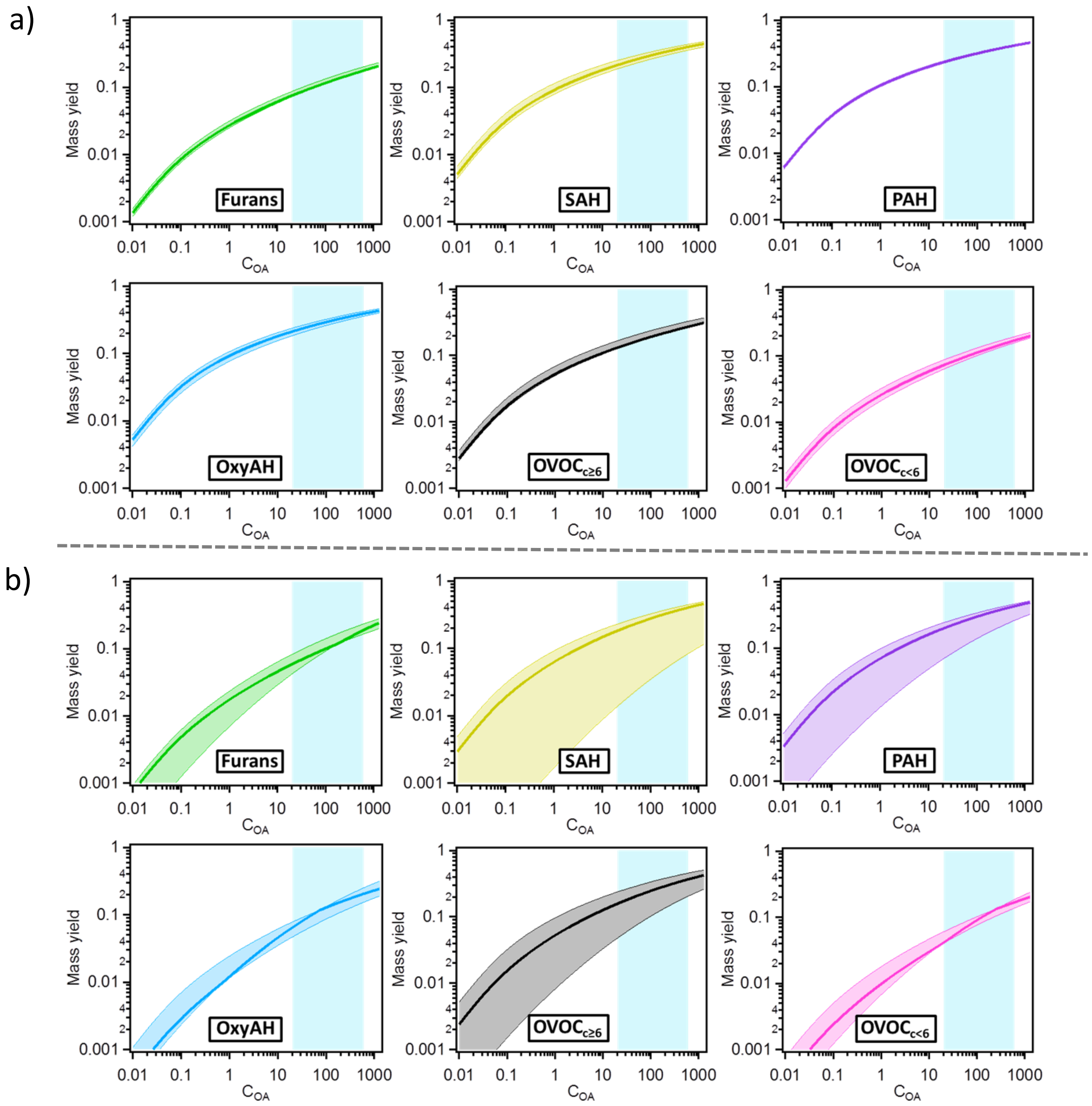

Figure S6. Mass yields for each class of compounds for Set1 (a) and Set2 (b). The solid lines represent the median values while the lower and upper limits are the 25th and 75th percentiles, respectively. The shaded background represent the experimental range (20-600 µg m^{-3}), outside this shaded area yields are extrapolated from the model.

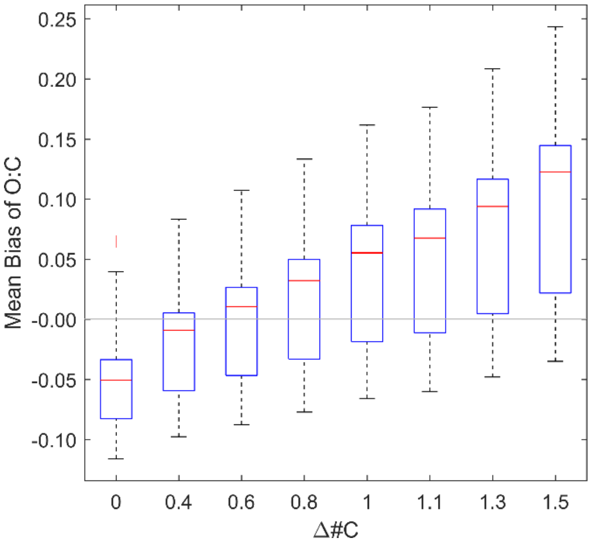

Figure S7. Mean bias of O:C ratio versus assumed ΔC.

Table S1. VOCs accounted as SOA precursor grouped in different chemical classes. Reported reaction rate constants (cm^3 $molec^{-1}$ s^{-1}) towards OH calculated from Set2 and towards NO_3 from NIST Database. Missing data are not available. Where there is ambiguity regarding the compound identity, the compound listed first is the one for which the NO_3 rate constant is reported. The *m/z* column denotes the *m/z* at which the species is actually observed in the PTR-TOF-MS (i.e., protonated mass) and the formula denotes the parent compound.

	m/z	Formula	Identified compound	k_{OH}	k_{NO3}
Furans	69.03	C4H4O	Furan	1.35×10^{-11}	1.4×10^{-12}
	83.05	C5H6O	2-Methylfuran	1.90×10^{-11}	1.1×10^{-11}
	85.03	C4H4O2	2-Furanone	4.91×10^{-12}	1.8×10^{-13}
	97.03	C5H4O2	Furan-2-carbaldehyde (furfural)	1.25×10^{-11}	2.6×10^{-12}
	97.06	C6H8O	2,3/2,4-/2,5-dimethylfuran	2.64×10^{-11}	5.8×10^{-11}/ 5.7×10^{-11}/ 5.8×10^{-11}
	99.04	C5H6O2	2-methyl-2-butenedial/ Furfuryl alcohol	9.87×10^{-12}	
	99.08	C6H10O	Dimethyldihydrofurane (Cyclohexanone)	9.53×10^{-13}	
	111.08	C7H10O	Trimethylfuran	2.47×10^{-11}	
	115.04	C5H6O3	4-Methoxy-2(5H)-furanone	6.89×10^{-13}	
	117.03	C8H4O	2,5-Diethynylfuran		
	119.05	C8H6O	Benzofuran		
	127.04	C6H6O3	5-(hydroxymethyl)furan-2-carbaldehyde/ Hydroxymethylfurfural	3.19×10^{-13}	
	141.05	C7H8O3	5-(Methoxymethyl)-2-furaldehyde		
	143.07	C7H10O3	2-Methyl-4,5-dihydro-furan-3-carboxylic acid methyl ester		
SAH	78.05	C6H5	Benzene fragment	4.45×10^{-13}	
	79.05	C6H6	Benzene	1.37×10^{-12}	1.4×10^{-17}
	93.07	C7H8	Toluene	4.85×10^{-12}	6.8×10^{-17}
	103.05	C8H6	Phenylacetylene	2.33×10^{-11}	
	105.07	C8H8	Styrene	4.12×10^{-11}	
	107.09	C8H10	Ethylbenzene/1,2-/1,3-/1,4-Xylene	1.25×10^{-11}	5.7×10^{-16}/ 2.0×10^{-16}/ 7.1×10^{-17}/ 1.5×10^{-16}
PAH	117.07	C9H8	1-indene	5.60×10^{-11}	
	119.09	C9H10	2-Phenylpropene/2,3-dihydro-1H-indene	6.59×10^{-11}	6.8×10^{-12}/ 6.0×10^{-15}
	129.07	C10H8	Naphtalene	2.14×10^{-11}	
	131.09	C10H10	Dihydronaphthalene		
	143.09	C11H10	Methylnaphtalene	3.81×10^{-11}	
	153.07	C12H8	Acenaphtylene	9.97×10^{-11}	5.4×10^{-12}
	155.09	C12H10	1,2-dihydro-Acenaphthylene	1.09×10^{-11}	4.6×10^{-13}
	157.10	C12H12	Dimethylnaphtalene	1.94×10^{-11}	
	167.09	C13H10	Fluorene	5.58×10^{-11}	3.5×10^{-14}

	179.09	C14H10	Phenanthrene	5.45×10^{-12}	
	193.10	C15H12	2-methylanthracene	2.70×10^{-10}	
	203.09	C16H10	Fluoranthrene	2.99×10^{-12}	
OxyAH	95.05	C6H6O	Phenol	2.51×10^{-11}	3.6×10^{-12}
	107.05	C7H6O	Benzaldehyde		2.0×10^{-15}
	109.07	C7H8O	Cresol (Methylphenol)	4.28×10^{-11}	1.5×10^{-11}
	111.04	C6H6O2	Benzenediol (Catechol)/ methylfurfural	1.23×10^{-11}	9.8×10^{-11}/ 5.4×10^{-12}
	121.07	C8H8O	2/3/4-methylbenzaldehyde/ Benzofuran, 2,3-dihydro		9.8×10^{-15}/ 9.5×10^{-15}/ 9.5×10^{-15}/ 1.1×10^{-13}
	123.04	C7H6O2	Hydroxy benzaldehyde		
	123.08	C8H10O	Xylenol (2,5-dimethyl phenol)	7.41×10^{-11}	3.3×10^{-11}
	125.06	C7H8O2	Methylbenzenediols/ Guaiacol (2-methoxyphenol)	2.15×10^{-11}	1.5×10^{-10}
	131.05	C9H6O	Indenone		
	133.07	C9H8O	Methylbenzofuran /Indanone		
	137.06	C8H8O2			
	137.10	C9H12O	2,4,6-Trimethyl phenol		
	139.04	C7H6O3	Salicylic acid		
	139.08	C8H10O2	1,2-/1,3-/1,4-Dimethoxybenzene	2.44×10^{-11}	
	147.04	C9H6O2	2-3-dihydroinden-1-one	9.10×10^{-12}	
	151.08	C9H10O2	4-Vinylguaiacol	6.72×10^{-12}	
	153.06	C8H8O3	4-hydroxy-3-methoxybenzaldehyde	4.20×10^{-11}	
	153.09	C9H12O2	4-ethyl-2-methoxyphenol/1,2-dimethoxy-4-methylbenzene		
	155.07	C8H10O3	Syringol/2,6-Dimethoxyphenol	2.07×10^{-11}	
	165.09	C10H12O2	2-methoxy-4-prop-1-enylphenol	2.92×10^{-11}	
	167.07	C9H10O3	1-(4-hydroxy-3-methoxyphenyl)ethanone/2,5-dimethylbenzaldehyde/3,4-dimethoxybenzaldehyde	6.70×10^{-12}	
	167.11	C10H14O2	2-methoxyphenol-4-propylphenol	2.46×10^{-11}	
	169.09	C9H12O3	2-6-dimethoxy-4-methylphenol	3.47×10^{-10}	
	183.07	C9H10O4	3-4-dimethoxybenzoic acid /4-hydroxy-3,5-dimethoxybenzaldehyde/ 4-ethyl-2,6-dimethoxyphenol	7.74×10^{-12}	
	183.10	C10H14O3	4-ethyl-2,6-dimethoxyphenol	2.07×10^{-11}	
	195.10	C11H14O3	1-3-dimethoxy-2-prop-2-enoxybenzene	3.81×10^{-12}	
	145.07	C10H8O	Naphtol	6.08×10^{-11}	
	181.07	C13H8O	Fluoren-9-one	-1.17×10^{-12}	
OVOCc≥6	94.04	C6H5O		4.84×10^{-11}	
	108.06	C7H7O	Phenoxymethyl	3.57×10^{-11}	
	109.03	C6H4O2	Benzoquinone	2.86×10^{-12}	
	110.04	C6H5O2	2-Hydroxyphenolate	1.66×10^{-11}	

	113.10	C7H12O	Cyclohexane-1-carboxaldehyde	-3.62×10^{-13}	3.2×10^{-14}
	115.08	C6H10O2		6.59×10^{-10}	
	117.09	C6H12O2	Hexanoic acid	2.06×10^{-12}	1.2×10^{-15}
	127.08	C7H10O2		1.73×10^{-11}	
	141.09	C8H12O2			
	145.04	C6H8O4	Dimethyl fumarate		
	147.08	C10H10O			
OVOCc<6	57.03	C3H4O	Acrolein	7.96×10^{-13}	1.1×10^{-15}
	71.05	C4H6O	Methyl venyl ketone/Methacrolein/Crotonaldehyde	1.51×10^{-11}	4.0×10^{-16}/ 5.5×10^{-15}/ 3.3×10^{-15}
	75.04	C3H6O2	Methyl acetate/Propionic acid	4.41×10^{-13}	7.0×10^{-18}/ 1.7×10^{-17}
	81.03	C5H4O	Cyclopentadienone	6.83×10^{-11}	
	85.06	C5H8O	3-methyl-3-buten-2-one	1.35×10^{-11}	
	87.04	C4H6O2	Vinyl acetate	2.46×10^{-12}	7.5×10^{-15}
	87.08	C5H10O	Pentanal	-2.67×10^{-13}	2.6×10^{-14}
	89.06	C4H8O2	ethyl acetate	1.20×10^{-12}	
	95.01	C5H2O2			
	96.02	C5H3O2			
	101.06	C5H8O2	2-Butenoic acid, methyl ester, (E)-/ 2-Propenoic acid, ethyl ester / Methyl methacrylate	1.61×10^{-12}	1.8×10^{-15}/ 1.7×10^{-16}/ 3.6×10^{-16}
	103.04	C4H6O3			
	103.04	C4H6O3		8.51×10^{-12}	
	103.08	C5H10O2	Butanoic acid, methyl ester/ 3-Hydroxy-3-methyl-2-butanone/n-Propyl acetate/ Propanoic acid, ethyl ester	1.27×10^{-12}	4.8×10^{-17}/ 2.0×10^{-16}/ 5.0×10^{-17}/ 3.3×10^{-17}
	117.06	C5H8O3	Levulinic acid	4.53×10^{-12}	

Table S2. Experimental conditions of published SOA yields for different compounds. Reported the type of reactor deployed and the experimental temperatures investigated (Odum et al., 1996; Takekawa et al., 2003; Johnson et al., 2005; Song et al., 2005; Ng et al., 2007; Henry et al., 2008; Chan et al., 2009; Gómez Alvarez et al., 2009; Shakya and Griffin, 2010; Chan et al., 2010; Nakao et al., 2011; Borrás and Tortajada-Genaro, 2012; Yee et al., 2013; Chen et al., 2016; Li et al., 2016; Ahlberg et al., 2017). Missing data are not specified in the related paper.

reference	**compound**	**reactor/chamber**	**temperature**
Ahlberg et al. (2017)	m-xylene	flow reactor	
Song et al. (2005)	m-xylene	smog chamber	27°C
Nakao et al. (2011)	m-xylene	smog chamber	27°C
	toluene	smog chamber	27°C
	benzene	smog chamber	27°C
	o-cresol	smog chamber	27°C
	m-cresol	smog chamber	27°C
	phenol	smog chamber	27°C
Ng et al. (2007)	m-xylene	smog chamber	25°C
	toluene	smog chamber	25°C
Li et al. (2016a)	m-xylene	smog chamber	27°C
	toluene	smog chamber	27°C
	benzene	smog chamber	27°C
	1,2,4-trimethylbenzene	smog chamber	27°C
	1,2,4,5-trimethylbenzene	smog chamber	27°C
Odum et al. (1996)	m-xylene	outdoor chamber	
	1,2,4-trimethylbenzene	outdoor chamber	
Takekawa et al. (2003)	m-xylene	smog chamber	9°C, 30°C
	toluene	smog chamber	9°C, 30°C
	1,2,4-trimethylbenzene	smog chamber	9°C, 30°C
Borras et al. (2012)	benzene	photoreactor	
	phenol	photoreactor	
	catechol	photoreactor	
Johnson et al. (2005)	benzene	outdoor chamber	23°C-32°C
	1,3,5-trimethylbenzene	outdoor chamber	19°C-31°C
Henry et al. (2008)	m-cresol	smog chamber	20°C-21°C
	p-cresol	smog chamber	20°C-21°C
	o-cresol	smog chamber	20°C-21°C
Yee et al. (2013)	phenol	smog chamber	20°C-26°C
	guaiacol	smog chamber	20°C-26°C
	syringol	smog chamber	20°C-26°C
Chan et al. (2009)	naphtalene	smog chamber	26°C
	1-methylnaphtalene	smog chamber	26°C
	2-methylnaphtalene	smog chamber	26°C
Chen et al. (2016)	naphtalene	smog chamber	
	1-methylnaphtalene	smog chamber	
	2-methylnaphtalene	smog chamber	
Shakya et al. (2010)	naphtalene	smog chamber	21°C-24°C

	methylnaphtalene	smog chamber	21°C-24°C
	acenaphtylene	smog chamber	21°C-24°C
	biphenyl	smog chamber	21°C-24°C
Chan et al. (2010)	methacrolein	smog chamber	20°C-21°C
	crotonaldehyde	smog chamber	20°C-21°C
	acrolein	smog chamber	20°C-21°C
	pentanal	smog chamber	20°C-21°C
Gomez Alvarez et al. (2009)	furan	smog chamber	25°C
	methylfuran	smog chamber	25°C
Li et al. (2016b)	1,2,3-trimethylbenzene	smog chamber	27°C
	1,2,5-trimethylbenzene	smog chamber	27°C

Table S3. OH reaction rate constants (k_{OH}) (cm^3 molec^{-1} s^{-1}) determined for each precursors class from Set2.

Expt.	Furans	SAH	PAH	OxyAH	OVOC$_{c\geq6}$	OVOC$_{c<6}$
1 (-10C)	1.34×10^{-11}	3.22×10^{-12}	2.43×10^{-11}	1.99×10^{-11}	1.16×10^{-11}	7.41×10^{-12}
2 (-10C)	2.19×10^{-11}	5.63×10^{-12}	5.74×10^{-11}	3.85×10^{-11}	3.38×10^{-11}	2.90×10^{-11}
3 (+15C)	8.41×10^{-12}	3.79×10^{-12}	3.48×10^{-11}	2.37×10^{-11}	9.24×10^{-12}	5.48×10^{-12}
4 (+15C)	8.91×10^{-12}	4.31×10^{-12}	3.33×10^{-11}	1.87×10^{-11}	1.16×10^{-11}	5.97×10^{-12}
5 (+15C)	1.36×10^{-11}	3.70×10^{-12}	1.92×10^{-11}	3.09×10^{-11}	1.19×10^{-11}	7.71×10^{-12}
6 (+15C)	1.22×10^{-11}	3.17×10^{-12}	2.96×10^{-11}	2.73×10^{-11}	1.00×10^{-11}	7.75×10^{-12}
7 (+15C)	8.52×10^{-12}	3.32×10^{-12}	3.10×10^{-11}	2.09×10^{-11}	8.94×10^{-12}	7.78×10^{-12}

Table S4. Molecular properties of VBS species assuming ΔC = 0.6 due to fragmentation. #C and #H are calculated as averaged values of all chemical species for each precursor category. #O of each precursor class and volatility bins are calculated by the SIMPOL approach (Pankow and Asher, 2008), provided by Eq. (3) in Donahue et al. (2011).

OA Species	**logC***	**#C**	**#O**	**#H**	**O:C**	**Molecular Weight**
POA	-1	11.00	4.11	18.24	0.374	216
	0	11.75	3.43	20.12	0.292	216
	1	12.50	2.73	22.32	0.218	216
	2	13.25	2.01	24.84	0.152	216
	3	14.00	1.27	26.68	0.091	215
	4	14.75	0.51	29.84	0.035	215
Furans	-1	5.53	5.15	6.13	0.932	155
	0	5.53	4.68	6.13	0.847	147
	1	5.53	4.21	6.13	0.761	140
	2	5.53	3.73	6.13	0.675	132
	3	5.53	3.25	6.13	0.588	124
	4	5.53	2.76	6.13	0.500	117
SAH	-1	6.77	4.95	6.77	0.731	167
	0	6.77	4.47	6.77	0.660	159
	1	6.77	3.99	6.77	0.589	152
	2	6.77	3.50	6.77	0.517	144
	3	6.77	3.00	6.77	0.444	136
	4	6.77	2.50	6.77	0.370	128
PAH	-1	11.52	3.99	9.50	0.347	212
	0	11.52	3.48	9.50	0.302	203
	1	11.52	2.96	9.50	0.257	195
	2	11.52	2.44	9.50	0.212	187
	3	11.52	1.91	9.50	0.166	178
	4	11.52	1.36	9.50	0.118	170
OxyAH	-1	8.17	4.69	8.72	0.574	182
	0	8.17	4.20	8.72	0.514	174
	1	8.17	3.71	8.72	0.454	166
	2	8.17	3.21	8.72	0.392	158
	3	8.17	2.70	8.72	0.330	150

	4	8.17	2.19	8.72	0.268	142
OCOC$_{C\geq6}$	-1	6.42	5.01	8.13	0.780	165
	0	6.42	4.53	8.13	0.706	158
	1	6.42	4.05	8.13	0.631	150
	2	6.42	3.57	8.13	0.556	142
	3	6.42	3.08	8.13	0.479	134
	4	6.42	2.58	8.13	0.402	126
OVOC$_{C<6}$	-1	4.00	5.37	5.76	1.342	140
	0	4.00	4.91	5.76	1.228	132
	1	4.00	4.45	5.76	1.113	125
	2	4.00	3.99	5.76	0.997	118
	3	4.00	3.52	5.76	0.880	110
	4	4.00	3.05	5.76	0.762	103

References

Ahlberg, E., Falk, J., Eriksson, A., Holst, T., Brune, W. H., Kristensson, A., Roldin, P. and Svenningsson, B.: Secondary organic aerosol from VOC mixtures in an oxidation flow reactor, Atmos. Environ., 161, 210–220, doi:10.1016/j.atmosenv.2017.05.005, 2017.

Borrás, E. and Tortajada-Genaro, L. A.: Secondary organic aerosol formation from the photo-oxidation of benzene, Atmos. Environ., 47, 154–163, doi:10.1016/j.atmosenv.2011.11.020, 2012.

Chan, A. W. H., Kautzman, K. E., Chhabra, P. S., Surratt, J. D., Chan, M. N., Crounse, J. D., Wennberg, P. O., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs), Atmos. Chem. Phys., 12, 2009.

Chan, A. W. H., Chan, M. N., Surratt, J. D., Chhabra, P. S., Loza, C. L., Crounse, J. D., Yee, L. D., Flagan, R. C., Wennberg, P. O. and Seinfeld, J. H.: Role of aldehyde chemistry and NOx concentrations in secondary organic aerosol formation, Atmos. Chem. Phys., 20, 2010.

Chen, C.-L., Kacarab, M., Tang, P. and Cocker, D. R.: SOA formation from naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene photooxidation, Atmos. Environ., 131, 424–433, doi:10.1016/j.atmosenv.2016.02.007, 2016.

Gómez Alvarez, E., Borrás, E., Viidanoja, J. and Hjorth, J.: Unsaturated dicarbonyl products from the OH-initiated photo-oxidation of furan, 2-methylfuran and 3-methylfuran, Atmos. Environ., 43(9), 1603–1612, doi:10.1016/j.atmosenv.2008.12.019, 2009.

Henry, F., Coeurtourneur, C., Ledoux, F., Tomas, A. and Menu, D.: Secondary organic aerosol formation from the gas phase reaction of hydroxyl radicals with m-, o- and p-cresol, Atmos. Environ., 42(13), 3035–3045, doi:10.1016/j.atmosenv.2007.12.043, 2008.

Johnson, D., Jenkin, M. E., Wirtz, K. and Martin-Reviejo, M.: Simulating the formation of secondary organic aerosol from the photooxidation of aromatic hydrocarbons, Environmental Chemistry, 2(1), 35, doi:10.1071/EN04079, 2005.

Li, L., Tang, P., Nakao, S. and Cocker III, D. R.: Impact of molecular structure on secondary organic aerosol formation from aromatic hydrocarbon photooxidation under low-NOx conditions, Atmos. Chem. Phys., 16(17), 10793–10808, doi:10.5194/acp-16-10793-2016, 2016.

Nakao, S., Clark, C., Tang, P., Sato, K. and Cocker III, D.: Secondary organic aerosol formation from phenolic compounds in the absence of NOx, Atmos. Chem. Phys., 11(20), 10649–10660, doi:10.5194/acp-11-10649-2011, 2011.

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7(14), 3909–3922, 2007.

NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, https://doi.org/10.18434/T4D303, (retrieved November 29, 2018).

Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C. and Seinfeld, J. H.: Gas/particle partitioning and secondary organic aerosol yields, 1996.

Shakya, K. M. and Griffin, R. J.: Secondary organic aerosol from photooxidation of polycyclic aromatic hydrocarbons, Environ. Sci. Technol., 44(21), 8134–8139, doi:10.1021/es1019417, 2010.

Song, C., Na, K. and Cocker, D. R.: Impact of the hydrocarbon to NOx ratio on secondary organic aerosol formation, Environ. Sci. Technol., 39(9), 3143–3149, doi:10.1021/es0493244, 2005.

Takekawa, H., Minoura, H. and Yamazaki, S.: Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, Atmos. Environ., 37(24), 3413–3424, doi:10.1016/S1352-2310(03)00359-5, 2003.

Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, M. N., Chan, A. W. H., Hersey, S. P., Crounse, J. D., Wennberg, P. O., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols, Atmos. Chem. Phys., 13(16), 8019–8043, doi:10.5194/acp-13-8019-2013, 2013.