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Formation of highly oxygenated organic molecules from aromatic compounds

Ugo Molteni et al.

Correspondence to: Urs Baltensperger (urs.baltensperger@psi.ch)

Section 1

Here a description of the OH generator and the involved reactions is given. A kinetic reaction model was developed to investigate the effect of uncertainties in the initial OH concentration on the oxidation product distribution.

The radiation at 172 nm excites molecular oxygen and water vapor triggering the following radical reactions:

$h\nu + O_2$	→	$O(^1D) + O(^3P)$	(R-C1)
$O(^1D) + M$	→	$O(^3P) + M$	(R-C2)
$O(^3P) + O_2 + M$	→	$O_3 + M$	(R-C3)
$O(^1D) + H_2O$	→	2 OH	(R-C4)
$h\nu + H_2O$	→	H + OH	(R-C5)
$H + O_2 + M$	→	$HO_2 + M$	(R-C6)
$OH + O_3$	→	$HO_2 + O_2$	(R-C7)
$HO_2 + O_3$	→	$OH + 2O_2$	(R-C8)
$OH + HO_2$	→	$H_2O + O_2$	(R-C9)
$HO_2 + HO_2$	→	$H_2O_2 + O_2$	(R-C10)
$H_2O_2 + OH$	→	$H_2O + HO_2$	(R-C11)

The humidified air flow is exposed to the 172 nm radiation for 50 ms and is then within 30 ms transferred to the mixing zone with the sample flow. The oxidant species produced are OH, HO_2, O_3 and H_2O_2. The final OH concentration entering the mixing zone depends on the residence time of the air in the lamp and in the transfer region.

The kinetic model includes 31 species and 36 reactions from the MCM 3.3.1 (Jenkin et al., 2003). Mesitylene is selected as ArHC for these simulations and its reaction mechanism is extended up to the second generation products. The model is run for 20 seconds in agreement with the residence time of the flow tube reactor with a simulation time resolution of 2 ms. The model is initiated with the measured concentrations of ozone ($3.45\ 10^{12}$ molecules cm^{-3} without mesitylene) and mesitylene ($2.46\ 10^{12}$ molecules cm^{-3} without lamp on) at the exit of the flow tube. The initial OH radical concentration ($8.50\ 10^{11}$ molecules cm^{-3}) is tuned in order to match the OH exposure, which was determined from the amount of reacted mesitylene. The initial HO_2 radical concentration ($1.70\ 10^{12}$ molecules cm^{-3}) is set at twice the initial OH radical concentration. Wall losses of about 35% are estimated for mesitylene HOMs but are not implemented in the model. Figure S1-1 shows the temporal evolution of 6 selected species: reacted mesitylene (T135MB reacted), HO_2 radical (HO2), OH radical (OH) as well as 3 products of the mesitylene oxidation with the OH radical (TM135BPRO2, TM135BPOOH and TM135B2OH). TM135BPRO2 is an intermediate peroxy radical after OH attack; TM135BPOOH is a product from the reaction of TM135BPRO2 with the HO_2 radical while TM135BPO2OH is a product from the reaction of TM135BPRO2 with a peroxy radical RO_2. Mesitylene reacted reaches a plateau after about 0.03 seconds while TM135BPRO2 reaches a maximum value around 0.01-0.02 seconds and then rapidly decreases. The closed shell products TM135BPOOH and TM135BPO2OH constantly increase and reach a plateau after about 0.4-1.0 seconds. A similar trend could be expected for HOMs assuming

that TM135BPRO2 undergoes an autoxidation chain and is terminated either by HO_2 or by RO_2. In a test run where the initial mesitylene concentration and the reaction rate constant towards OH radicals were doubled, the ratio TM135BPOOH/TM135BPO2OH varied only by about 18%.

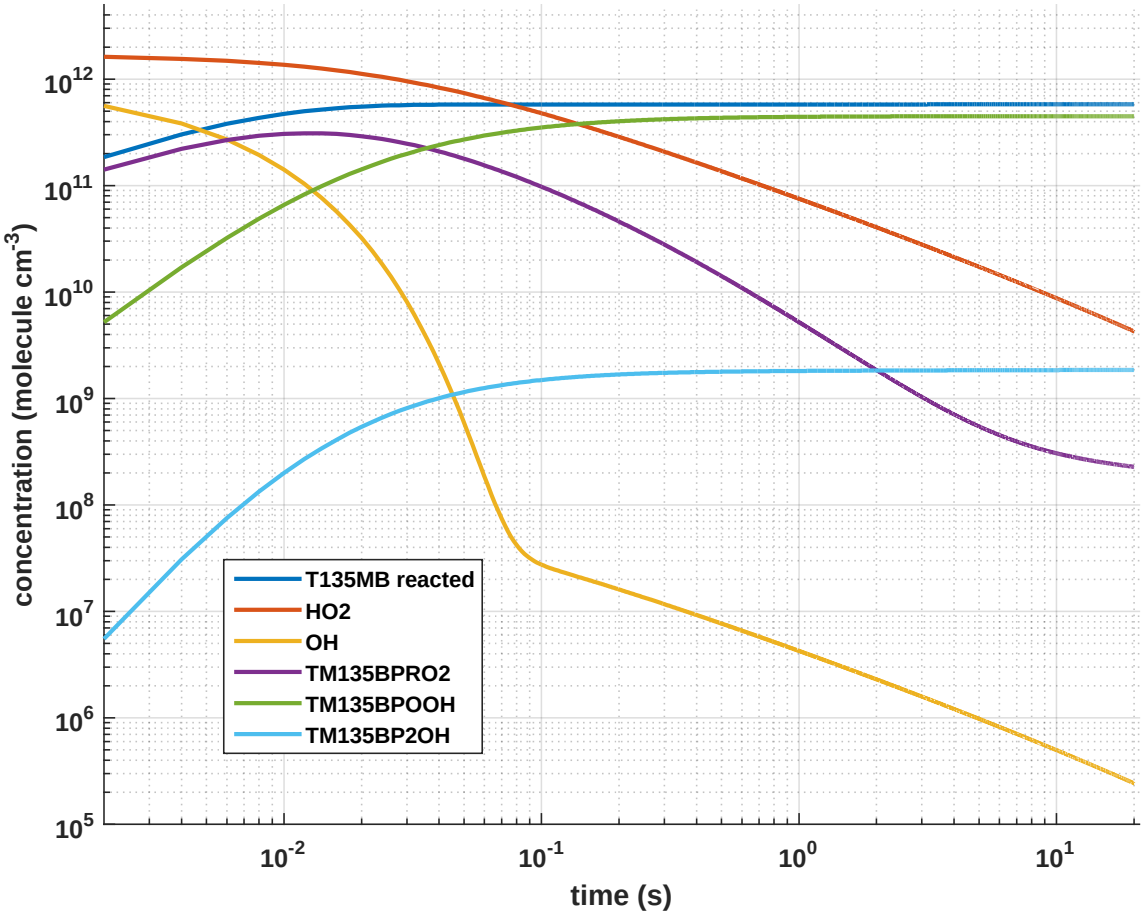

Figure S1-1. Temporal evolution of selected species according to the mesitylene flow tube kinetic model.

Section 2

Peak lists of the most abundant HOMs of each ArHC tested are presented in the next 7 tables. The peaks are sorted according to decreasing relative intensity. Chemical formula, mass-to-charge ratio (Th) and fraction of the explained signal are included. The mass-to-charge ratio includes the mass of NO_3 if present.

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Table S2-1

CI-APi-TOF peak list for benzene (C_6H_6) oxidation products.

Chemical formula	Mass-to-charge ratio (Th)	Fraction of explained signal
$C_6H_8O_5(NO_3)^-$	222.0255	14.1
$C_5H_6O_8(NO_3)^-$	255.9946	11.0
$C_6H_6O_2(NO_3)^-$	172.0251	10.0
$C_{12}H_{14}O_8(NO_3)^-$	348.0572	6.1
$C_5H_6O_7(NO_3)^-$	239.9997	3.0
$C_6H_8O_9(NO_3)^-$	286.0052	2.6
$C_5H_6O_6(NO_3)^-$	224.0048	2.6
$C_6H_8O_6(NO_3)^-$	238.0205	2.3
$C_6H_8O_8(NO_3)^-$	270.0103	1.8
$C_{12}H_{14}O_{14}(NO_3)^-$	444.0267	1.8
$C_6H_8O_{10}(NO_3)^-$	302.0001	1.8
$C_6H_6O_4(NO_3)^-$	204.0150	1.8
$C_6H_8O_7(NO_3)^-$	254.0154	1.7
$C_6H_{10}O_6(NO_3)^-$	240.0361	1.5
$C_{12}H_{14}O_{12}(NO_3)^-$	412.0369	1.3
$C_6H_7O_9(NO_3)^-$	284.9974	1.1
$C_6H_7O_4^-$	143.0350	1.1
$C_{12}H_{16}O_9(NO_3)^-$	366.0678	1.0
$C_6H_8O_4(NO_3)^-$	206.0306	0.8
$C_6H_6O_5(NO_3)^-$	220.0099	0.8
$C_{12}H_{14}O_9(NO_3)^-$	364.0522	0.8
$C_6H_6O_6(NO_3)^-$	236.0048	0.8
$C_5H_6O_2(NO_3)^-$	160.0251	0.7
$C_{12}H_{14}O_{10}(NO_3)^-$	380.0471	0.7
$C_6H_5O_5^-$	157.0143	0.7
$C_{12}H_{16}O_8(NO_3)^-$	350.0729	0.6
$C_6H_5O_6^-$	173.0092	0.6
$C_5H_8O_7(NO_3)^-$	242.0154	0.6
$C_6H_{10}O_8(NO_3)^-$	272.0259	0.6
$C_5H_6O_5(NO_3)^-$	208.0099	0.6
$C_{12}H_{14}O_{11}(NO_3)^-$	396.0420	0.5

$C_{12}H_{12}O_{13}(NO3)^-$	426.0161	0.5
$C_6H_7O_6^-$	175.0248	0.5
$C_{10}H_{10}O_{18}(NO_3)^-$	479.9751	0.5
$C_6H_7O_4(NO_3)^-$	205.0228	0.4
$C_6H_6O_7(NO_3)^-$	251.9997	0.4

Table S2-2

CI-APi-TOF peak list for toluene (C_7H_8) oxidation products.

Chemical formula	Mass-to-charge ratio (Th)	Fraction of explained signal
$C_7H_{10}O_9(NO_3)^-$	300.0208	12.4
$C_{14}H_{18}O_{12}(NO_3)^-$	440.0682	10.2
$C_7H_{10}O_5(NO_3)^-$	236.0412	6.8
$C_7H_{10}O_7(NO_3)^-$	268.0310	6.3
$C_{14}H_{18}O_8(NO_3)^-$	376.0885	6.1
$C_7H_{10}O_8(NO_3)^-$	284.0259	6.0
$C_7H_{10}O_6(NO_3)^-$	252.0361	3.7
$C_7H_8O_2(NO_3)^-$	186.0408	2.8
$C_{14}H_{18}O_{10}(NO_3)^-$	408.0784	2.5
$C_7H_{12}O_8(NO_3)^-$	286.0416	2.3
$C_{14}H_{18}O_9(NO_3)^-$	392.0834	1.7
$C_6H_7O_6(NO_3)^-$	237.0126	1.5
$C_7H_{12}O_7(NO_3)^-$	270.0467	1.4
$C_{14}H_{18}O_{11}(NO_3)^-$	424.0733	1.4
$C_7H_9O_9(NO_3)^-$	299.0130	1.3
$C_7H_{10}O_{11}(NO_3)^-$	332.0107	1.2
$C_7H_9O_{11}(NO_3)^-$	331.0029	1.1
$C_6H_6O_5^-$	158.0215	1.1
$C_{14}H_{20}O_{11}(NO_3)^-$	426.0889	1.1
$C_{14}H_{20}O_9(NO_3)^-$	394.0991	1.0
$C_7H_8O_4(NO_3)^-$	218.0306	1.0
$C_6H_8O_8(NO_3)^-$	270.0103	1.0
$C_{14}H_{18}O_{14}(NO_3)^-$	472.0580	1.0
$C_7H_{10}O_{10}(NO_3)^-$	316.0158	1.0
$C_7H_{12}O_6(NO_3)^-$	254.0518	0.8
$C_7H_8O_5(NO_3)^-$	234.0255	0.8
$C_7H_8O_6(NO_3)^-$	250.0205	0.8
$C_{14}H_{20}O_{10}(NO_3)^-$	410.0940	0.7
$C_7H_8O_8(NO_3)^-$	282.0103	0.7

Table S2-3

CI-APi-TOF peak list for ethylbenzene (C_8H_{10}) oxidation products.

Chemical formula	Mass-to-charge ratio (Th)	Fraction of explained signal
$C_8H_{12}O_7(NO_3)^-$	282.0467	8.7
$C_8H_{12}O_5(NO_3)^-$	250.0568	6.1
$C_{16}H_{22}O_8(NO_3)^-$	404.1198	5.9
$C_{16}H_{22}O_{12}(NO_3)^-$	468.0995	5.6
$C_{16}H_{22}O_{10}(NO_3)^-$	436.1096	4.9
$C_8H_{12}O_9(NO_3)^-$	314.0365	4.5
$C_8H_{12}O_6(NO_3)^-$	266.0518	4.4
$C_8H_9O_8^-$	233.0303	3.5
$C_8H_{12}O_8(NO_3)^-$	298.0416	3.4
$C_8H_9O_6^-$	201.0405	2.3
$C_8H_{10}O_6(NO_3)^-$	264.0361	1.9
$C_8H_{10}O_{10}(NO_3)^-$	328.0158	1.8
$C_8H_{14}O_7(NO_3)^-$	284.0623	1.7
$C_{16}H_{22}O_9(NO_3)^-$	420.1147	1.6
$C_8H_{10}O_8(NO_3)^-$	296.0259	1.6
$C_8H_{14}O_8(NO_3)^-$	300.0572	1.5
$C_{16}H_{20}O_9(NO_3)^-$	418.0991	1.4
$C_{16}H_{22}O_{14}(NO_3)^-$	500.0893	1.4
$C_{16}H_{22}O_{11}(NO_3)^-$	452.1046	1.3
$C_8H_{10}O_2(NO_3)^-$	200.0564	1.3
$C_{16}H_{24}O_9(NO_3)^-$	422.1304	1.2
$C_8H_9O_4^-$	169.0506	1.2
$C_8H_{10}O_9(NO_3)^-$	312.0208	1.1
$C_8H_{10}O_7(NO_3)^-$	280.0310	1.1
$C_8H_{12}O_{11}(NO_3)^-$	346.0263	1.0
$C_8H_{12}O_{10}(NO_3)^-$	330.0314	1.0
$C_8H_{11}O_6^-$	203.0561	0.9
$C_{16}H_{24}O_{11}(NO_3)^-$	454.1202	0.9
$C_7H_8O_5^-$	172.0377	0.9
$C_8H_9O_3^-$	153.0557	0.8
$C_8H_{14}O_6(NO_3)^-$	268.0674	0.8
$C_8H_8O_5^-$	184.0377	0.7
$C_{16}H_{24}O_{10}(NO_3)^-$	438.1253	0.7
$C_8H_{10}O_4(NO_3)^-$	232.0463	0.7
$C_7H_8O_5(NO_3)^-$	234.0255	0.7
$C_8H_{11}O_9(NO_3)^-$	313.0287	0.7
$C_7H_7O_4^-$	155.0350	0.6

Table S2-4

CI-APi-TOF peak list for xylene (C_8H_{10}) oxidation products.

Chemical formula	Mass-to-charge ratio (Th)	Fraction of explained signal
$C_{16}H_{22}O_8(NO_3)^-$	404.1198	18.0
$C_8H_{12}O_5(NO_3)^-$	250.0568	12.9
$C_8H_{12}O_6(NO_3)^-$	266.0518	8.9
$C_8H_{12}O_7(NO_3)^-$	282.0467	7.6
$C_{16}H_{22}O_{10}(NO_3)^-$	436.1096	4.3
$C_8H_{14}O_8(NO_3)^-$	300.0572	3.5
$C_8H_{14}O_7(NO_3)^-$	284.0623	3.3
$C_{16}H_{22}O_9(NO_3)^-$	420.1147	2.5
$C_8H_{12}O_8(NO_3)^-$	298.0416	2.2
$C_{16}H_{22}O_{12}(NO_3)^-$	468.0995	2.0
$C_8H_9O_4^-$	169.0506	1.7
$C_8H_{12}O_9(NO_3)^-$	314.0365	1.7
$C_8H_{14}O_6(NO_3)^-$	268.0674	1.6
$C_{16}H_{24}O_{11}(NO_3)^-$	454.1202	1.4
$C_8H_{11}O_6(NO_3)^-$	265.0439	1.4
$C_{16}H_{22}O_{11}(NO_3)^-$	452.1046	1.2
$C_8H_{10}O_6(NO_3)^-$	264.0361	1.1
$C_8H_{10}O_8(NO_3)^-$	296.0259	1.0
$C_{16}H_{24}O_{10}(NO_3)^-$	438.1253	1.0
$C_8H_{10}O_5(NO_3)^-$	248.0412	0.9
$C_8H_{13}O_8(NO_3)^-$	299.0494	0.9
$C_8H_{10}O_7(NO_3)^-$	280.0310	0.8

Table S2-5

CI-APi-TOF peak list for mesitylene (C_9H_{12}) oxidation products.

Chemical formula	Mass-to-charge ratio (Th)	Fraction of explained signal
$C_{18}H_{26}O_8(NO_3)^-$	432.1511	24.2
$C_9H_{14}O_7(NO_3)^-$	296.0623	9.6
$C_9H_{14}O_6(NO_3)^-$	280.0674	8.2
$C_{18}H_{26}O_{10}(NO_3)^-$	464.1410	7.0
$C_9H_{16}O_7(NO_3)^-$	298.0780	4.6
$C_9H_{14}O_5(NO_3)^-$	264.0725	4.0
$C_9H_{16}O_8(NO_3)^-$	314.0729	3.3
$C_9H_{16}O_9(NO_3)^-$	330.0679	3.0
$C_9H_{13}O_7(NO_3)^-$	295.0545	3.0
$C_9H_{13}O_6^-$	217.0718	2.5
$C_9H_{15}O_8(NO_3)^-$	313.0651	1.7
$C_{18}H_{26}O_9(NO_3)^-$	448.1461	1.6
$C_9H_{14}O_8(NO_3)^-$	312.0572	1.5
$C_9H_{12}O_6(NO_3)^-$	278.0518	1.5
$C_9H_{17}O_{10}(NO_3)^-$	347.0705	1.3
$C_9H_{14}O_{10}^-$	282.0592	1.2
$C_9H_{17}O_9(NO_3)^-$	331.0756	1.2

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Table S2-6

CI-APi-TOF peak list for naphthalene ($C_{10}H_8$) oxidation products.

Chemical formula	Mass-to-charge ratio (Th)	Fraction of explained signal
$C_{20}H_{18}O_4(NO_3)^-$	384.1089	26.1
$C_{20}H_{18}O_6(NO_3)^-$	416.0987	17.4
$C_{20}H_{18}O_5(NO_3)^-$	400.1038	4.1
$C_{10}H_7O_5^-$	207.0299	3.5
$C_{20}H_{18}O_7(NO_3)^-$	432.0936	3.0
$C_{20}H_{18}O_9(NO_3)^-$	464.0834	2.9
$C_{10}H_{10}O_4(NO_3)^-$	256.0463	2.5
$C_{10}H_{10}O_5(NO_3)^-$	272.0412	2.1
$C_{10}H_7O_3^-$	175.0401	1.8
$C_{10}H_{10}O_8(NO_3)^-$	320.0259	1.7
$C_{20}H_{18}O_8(NO_3)^-$	448.0885	1.6
$C_{10}H_{10}O_6(NO_3)^-$	288.0361	1.5
$C_{10}H_8O_7(NO_3)^-$	302.0154	1.2
$C_{20}H_{20}O_7(NO_3)^-$	434.1093	1.1
$C_{10}H_7O_4^-$	191.0350	1.0
$C_{20}H_{18}O_{10}(NO_3)^-$	480.0784	1.0
$C_{20}H_{18}O_{11}(NO_3)^-$	496.0733	1.0
$C_{10}H_{12}O_6(NO_3)^-$	290.0518	0.9
$C_{10}H_{10}O_7(NO_3)^-$	304.0310	0.9
$C_{10}H_7O_6^-$	223.0248	0.9
$C_{10}H_7O_7^-$	239.0197	0.9
$C_{10}H_8O_5(NO_3)^-$	270.0255	0.9
$C_{10}H_{10}O_{10}(NO_3)^-$	352.0158	0.8
$C_{10}H_{10}O_9(NO_3)^-$	336.0208	0.6

Table S2-7

CI-APi-TOF peak list for biphenyl ($C_{12}H_{10}$) oxidation products.

Chemical formula	Mass-to-charge ratio (Th)	Fraction of explained signal
$C_{24}H_{22}O_8(NO_3)^-$	500.1198	9.1
$C_{12}H_{12}O_5(NO_3)^-$	298.0569	6.2
$C_{12}H_{14}O_6(NO_3)^-$	316.0674	5.6
$C_{24}H_{22}O_7(NO_3)^-$	484.1249	4.9
$C_{24}H_{24}O_7(NO_3)^-$	486.1406	3.7
$C_{12}H_9O_4^-$	217.0506	3.6
$C_{12}H_9O_3^-$	201.0557	3.5
$C_{24}H_{22}O_6(NO_3)^-$	468.1300	3.5
$C_{24}H_{22}O_9(NO_3)^-$	516.1147	3.2
$C_{24}H_{24}O_9(NO_3)^-$	518.1304	2.9
$C_{24}H_{24}O_8(NO_3)^-$	502.1355	2.8
$C_{24}H_{22}O_{11}(NO_3)^-$	548.1046	2.5
$C_{12}H_{12}O_6(NO_3)^-$	314.0518	2.4
$C_{12}H_{12}O_8(NO_3)^-$	346.0416	2.3
$C_{12}H_{14}O_5(NO_3)^-$	300.0725	1.7
$C_{12}H_{14}O_7(NO_3)^-$	332.0623	1.7
$C_{12}H_{12}O_7(NO_3)^-$	330.0467	1.4
$C_{24}H_{22}O_{10}(NO_3)^-$	532.1097	1.4
$C_{12}H_{12}O_9(NO_3)^-$	362.0365	1.4
$C_{11}H_9O_3^-$	189.0557	1.4
$C_{12}H_9O_5^-$	233.0455	1.2
$C_{12}H_{10}O_4^-$	218.0585	1.1
$C_{24}H_{24}O_{10}(NO_3)^-$	534.1253	1.1
$C_{24}H_{24}O_5(NO_3)^-$	454.1507	1.1
$C_{24}H_{22}O_{12}(NO_3)^-$	564.0995	1.1
$C_{24}H_{21}O_8^-$	437.1242	1.0
$C_{12}H_{12}O_4(NO_3)^-$	282.0619	1.0
$C_{12}H_{11}O_4^-$	219.0663	1.0
$C_{10}H_9O_2^-$	161.0608	0.8
$C_{12}H_{10}O_2(NO_3)^-$	248.0564	0.8
$C_{36}H_{34}O_{10}(NO_3)^-$	688.2036	0.8
$C_{12}H_{11}O_5^-$	235.0612	0.7
$C_{12}H_{10}O_4(NO_3)^-$	280.0463	0.7
$C_{11}H_7O_2^-$	171.0452	0.7
$C_{24}H_{22}O_5(NO_3)^-$	452.1351	0.6
$C_{10}H_7O_3^-$	175.0401	0.6
$C_{10}H_7O_4^-$	191.0350	0.6

Section 3

65 HOMs from the 7 tested compounds are presented in the next figures. Top panel left: pie chart showing the monomer and dimer fraction; 3 bar plots presenting the relative signal intensities for radicals, monomer and dimers. In the bar plots, the x-axis presents the number of oxygen atoms and the colour code the number of hydrogen atoms for each of the HOMs.

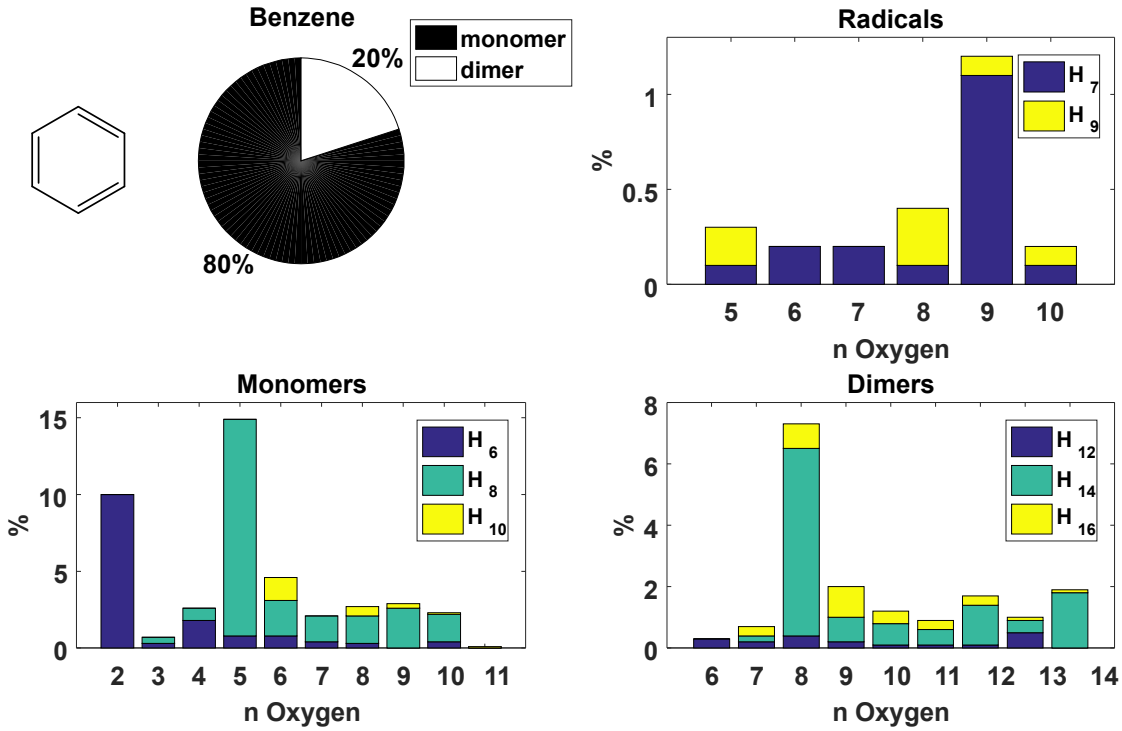

Figure S3-1 Benzene

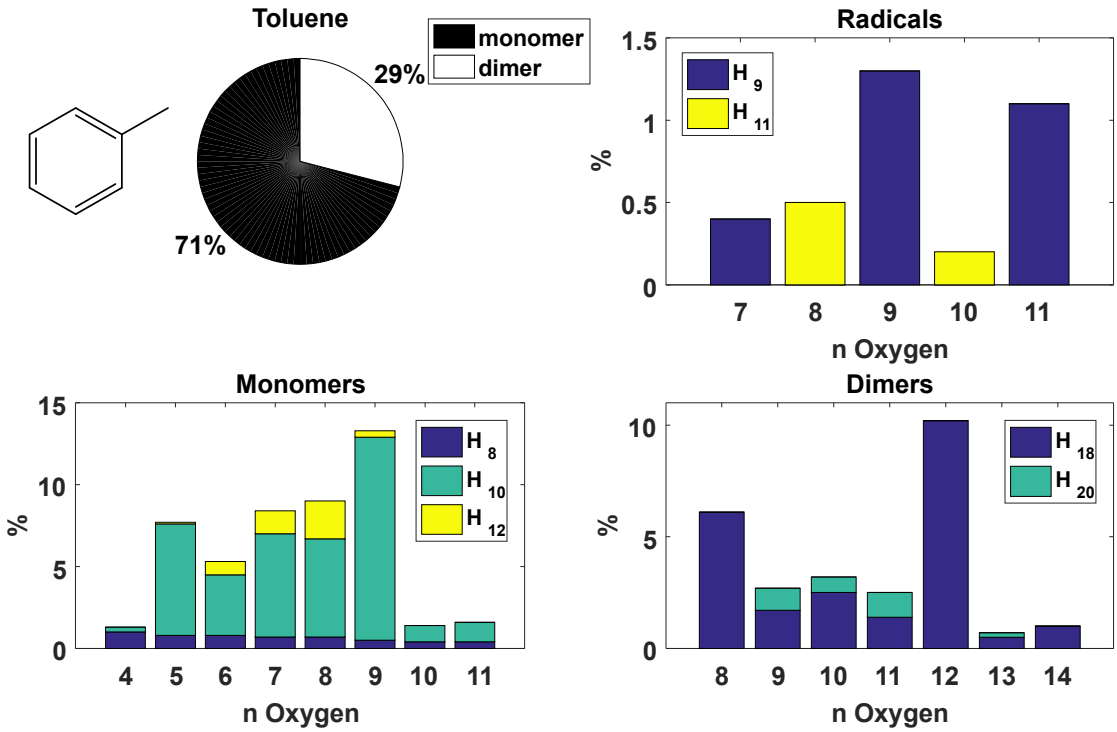

Figure S3-2 Toluene

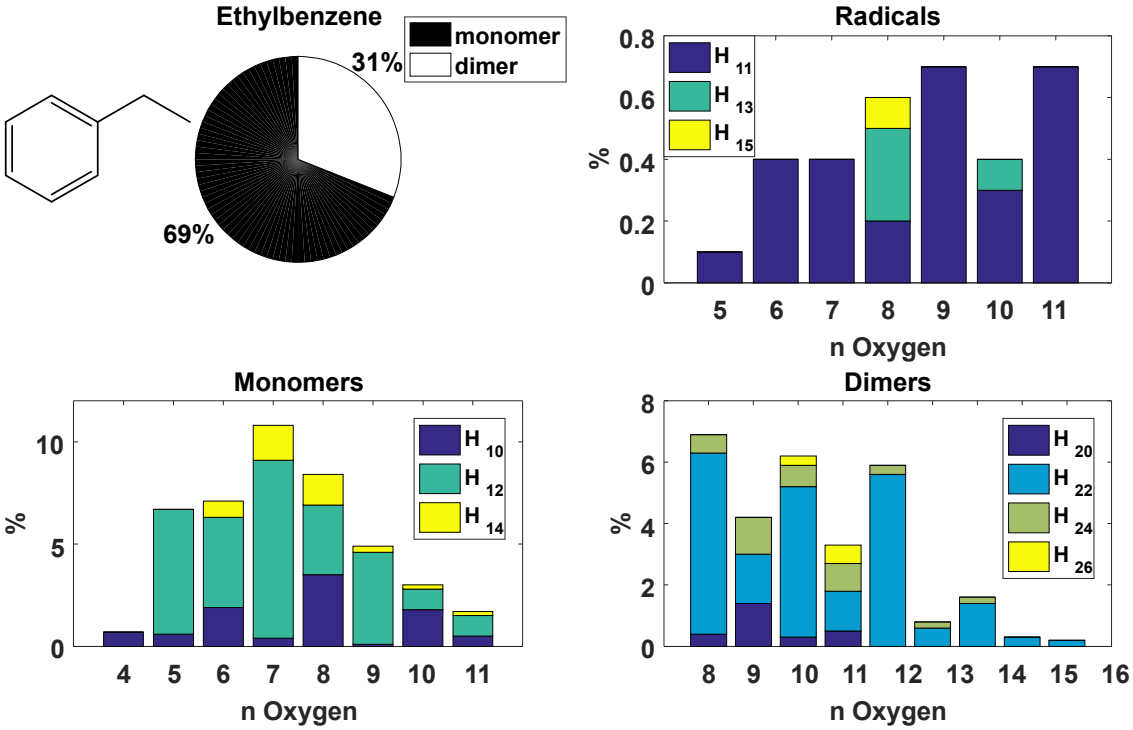

Figure S3-3 Ethylbenzene

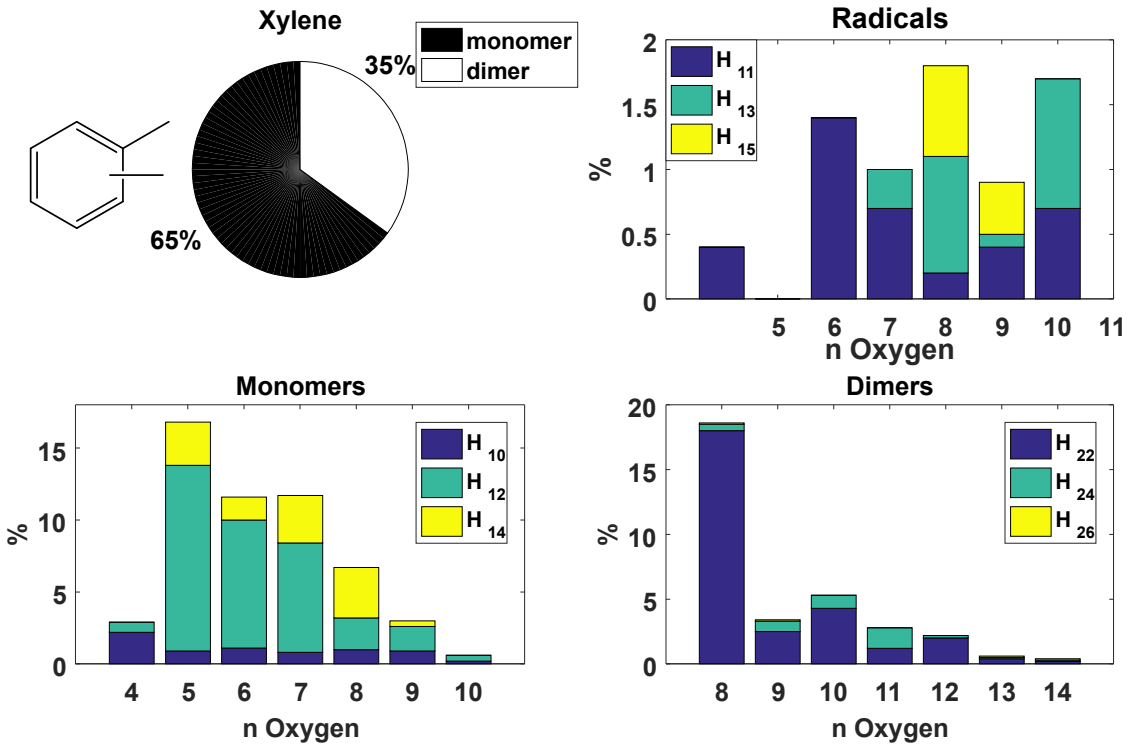

Figure S3-4 Xylene

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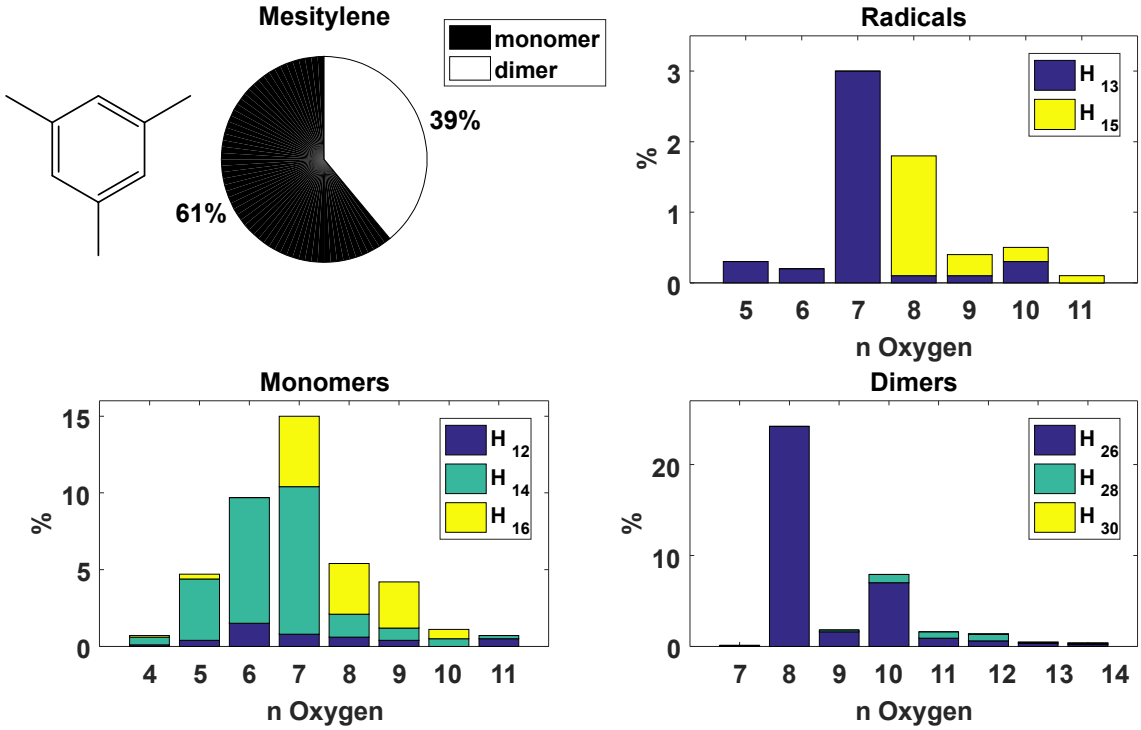

Figure S3-5 Mesitylene

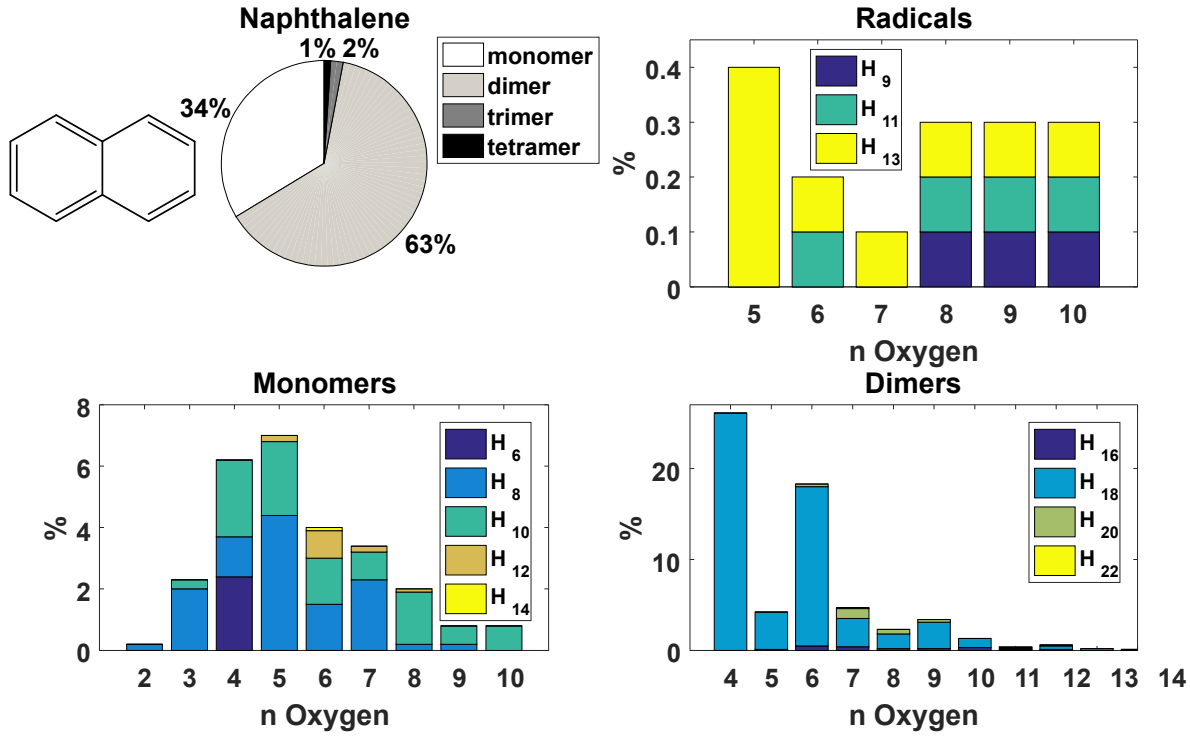

Figure S3-6 Naphthalene

85

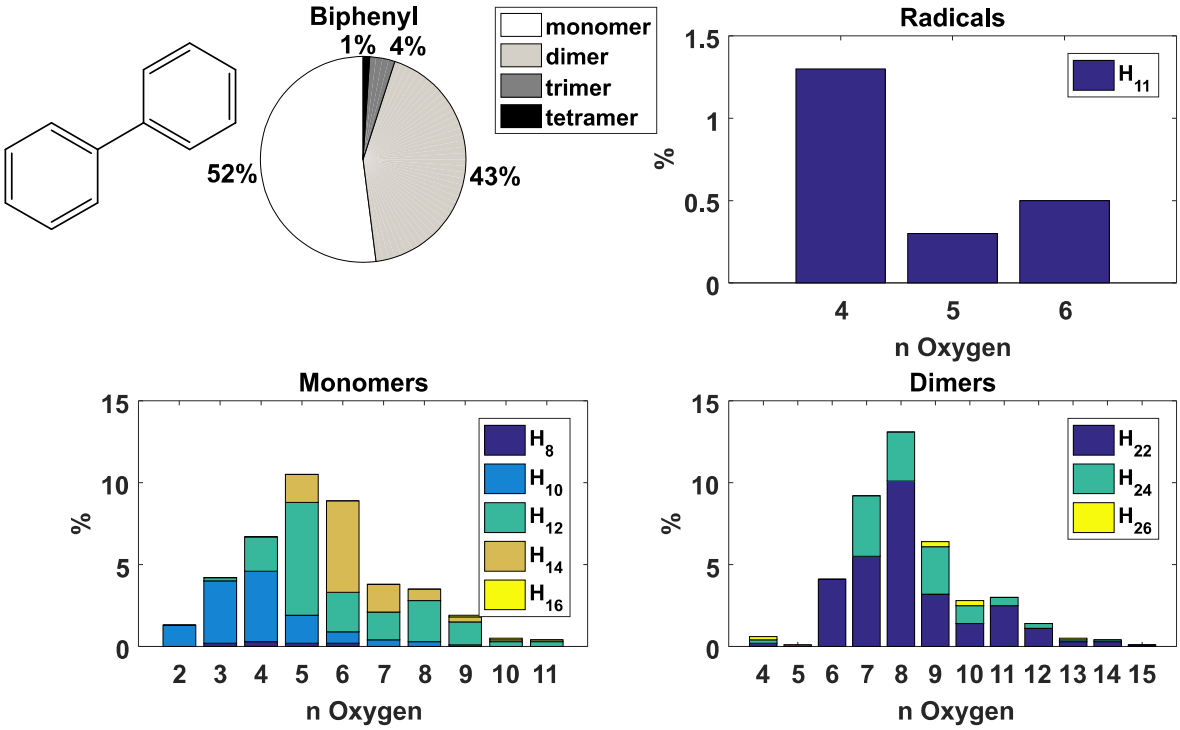

Figure S3-7 Biphenyl

References

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