

Supporting Information

Light-absorbing oligomer formation in secondary organic aerosol from reactive uptake of isoprene epoxydiols

Ying-Hsuan Lin^a, Sri Hapsari Budisulistiorini^a, Kevin Chu^a, Richard A. Siejack^b, Haofei Zhang^{a,c},
Matthieu Riva^a, Zhenfa Zhang^a, Avram Gold^a, Kathryn E. Kautzman^{b,*}, and Jason D. Surratt^{a,*}

^a Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA

^b Department of Chemistry, Towson University, Towson, MD 21252, USA

^c Present address: Department of Environmental Science, Policy and Management, University of California, Berkeley, CA 94720, USA

* To whom correspondence should be addressed.

Jason D. Surratt, Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA. Tel: (919)-966-0470; Fax: (919)-966-7911; Email: surratt@unc.edu
Kathryn E. Kautzman, Department of Chemistry, Towson University, Towson, MD 21252, USA
Tel: (410)-704-3046; Fax: (410)-704-4265; E-mail: kkautzman@towson.edu

The authors declare no conflict of interest.

For Submission To: Environmental Science & Technology

This supporting information contains 13 pages: 2 tables and 6 figures.

Quality assurance for experimental procedures of aerosol sample collection followed by offline chemical analyses.

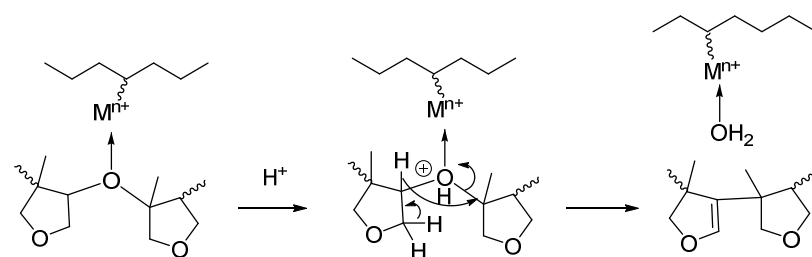
Quality assurance of experimental procedures was accomplished through a series of blank and control experiments. Seed-only and IEPOX-only experiments were preformed to ensure that browning occurs only from the heterogeneous uptake of IEPOX onto seed aerosols. These control experiments displayed no evidence of browning. Additionally, blank filters extracted for analysis by UV-Vis, UPLC/DAD-ESI-HR-QTOFMS, GC/MS, and FTIR did not demonstrate any artifacts or background signals in any of the analysis preformed. In order to assess if browning occurred as a function of filter storage time, we analyzed multiple aerosol samples collected from IEPOX reactive uptake experiments under low-RH conditions in the presence of acidified MgSO_4 seed. All filters were visibly brown at the end of sampling, suggesting that brown carbon was formed by in situ heterogeneous and multiphase reactions in the chamber experiments, rather than the sample storage phase. Filter samples analyzed immediately, 24 h after extraction, or following longer storage times showed similar MAC intensities and band shapes, again indicating that the sample storage time does not introduce artifacts in sample analysis.

Additional mechanistic discussion and alternative pathways. Regarding the elimination of bridging oxygens of the polyether, we are proposing a dehydrative coupling mechanism. As is the case for the pathway leading to cyclodehydration of the initial IEPOX oligomer, the mechanism is speculative (tentative). The proposal is based on the following observations from the literature: The dehydration of ethers is known and has been documented to occur both under strong acid conditions (Amberlyst 15)¹ and on coordination of ethers to metal ions.² The transient moieties from acid catalyzed dehydration in the chamber experiment may be held in proximity by coordination to Mg^{2+} to facilitate coupling to form a C – C bond.³ As noted above,

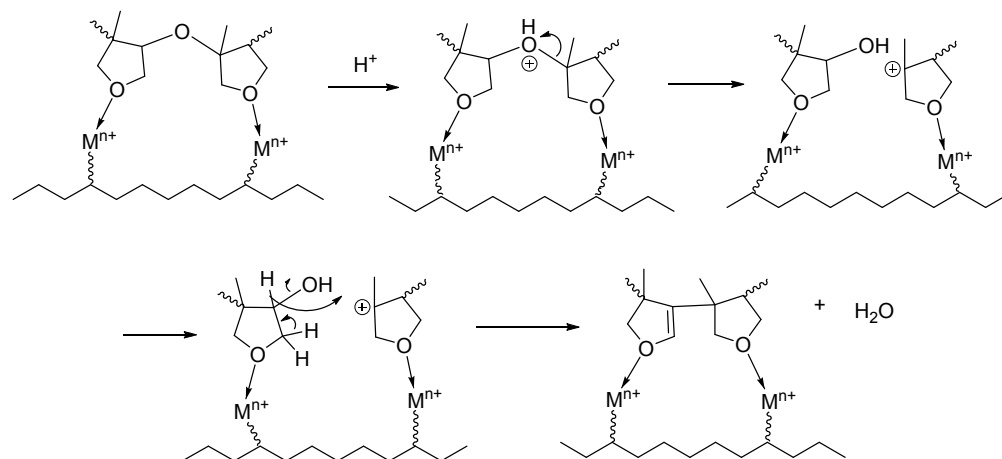
extremely low pH may occur in ambient aerosols along with metal ions or viscous particle coatings in the urban mix, which may similarly serve to maintain reacting moieties in close proximity. Observation of identical oligomers in chamber and field samples supports this suggestion.

Two alternative pathways are illustrated below based on coordination with a metal ion ($M^{n+} = Mg^{2+}$ in the chamber studies).

Pathway 1



Pathway 2



Description of Field Sites and $PM_{2.5}$ Sampling during the 2013 Southern Oxidant and Aerosol Study (SOAS). 2013 SOAS $PM_{2.5}$ samples presented in this paper were collected from Centreville, Alabama (AL), and Look Rock, Tennessee (TN). Centreville, AL is a rural site located ~85 km south-southwest of Birmingham and 50 km south of Tuscaloosa. Its surrounding is heavily populated with mixed deciduous (oak-hickory) and loblolly pine.⁴ Previous studies

showed that PM_{2.5} mass enhanced with the increase of organic matter (OM) during summer season,⁵ and isoprene-derived SOA tracers (i.e. 2-methyltetrols) contributed to 0.29-0.96% of total OM.⁶ Look Rock, TN is located on a ridge top of about 600 m above the surrounding valley terrain to the west and north, near the western boundary of Great Smoky Mountains National Park,⁷ which is a background site located south of Maryville and Knoxville. Previous studies suggested that PM_{2.5} mass at Look Rock, TN is largely contributed by organic and sulfate in all seasons,⁷ and its composition has a high OM/OC ratio (2.1), which is suggested due to more water-soluble components present in the organic aerosol.⁸ At each site, PM_{2.5} samples were collected onto pre-baked 8 × 10 inches Tissuquartz™ Filters (Pall Life Sciences) with Tisch high-volume PM_{2.5} air samplers operated at 1 m³ min⁻¹ for 23 h (i.e. 08:00 to 07:00 the next day). Filter samples were collected daily throughout the SOAS campaign (June 1, 2013-July 15, 2013), and stored at -20°C until analysis. Field blanks were collected weekly by placing pre-baked filters into the sampler for 15 min, and stored and analyzed in the same manner as the field samples. No light-absorbing oligomers were observed in the field blanks, indicating these compounds are associated with the PM_{2.5} samples collected from these sites.

References

- (1) Ronchin, L.; Vavasori, A.; Toniolo, L., Acid catalyzed alkylation of phenols with cyclohexene: Comparison between homogeneous and heterogeneous catalysis, influence of cyclohexyl phenyl ether equilibrium and of the substituent on reaction rate and selectivity. *J. Mol. Catal. A: Chem.* **2012**, 355 (0), 134-141.
- (2) Allison, J.; Ridge, D.P., The gas-phase chemistry of chlorotitanium ions with oxygen-containing organic compounds. *J. Am. Chem. Soc.* **1978**, 100 (1), 163-169.

(3) Shvartsburg, A.A., Gas-phase metal trications in protic solvent complexes. *J. Am. Chem. Soc.* **2002**, *124* (27), 7910-7911.

(4) Hansen, D.A.; Edgerton, E.S.; Hartsell, B.E.; Jansen, J.J.; Kandasamy, N.; Hidy, G.M.; Blanchard, C.L., The southeastern aerosol research and characterization study: Part 1-overview. *J. Air Waste Manag. Assoc.* **2003**, *53* (12), 1460-1471.

(5) Zheng, M.; Cass, G.R.; Schauer, J.J.; Edgerton, E.S., Source apportionment of PM_{2.5} in the Southeastern United States using solvent-extractable organic compounds as tracers. *Environ. Sci. Technol.* **2002**, *36* (11), 2361-2371.

(6) Clements, A.L.; Seinfeld, J.H., Detection and quantification of 2-methyltetrols in ambient aerosol in the southeastern United States. *Atmos. Environ.* **2007**, *41* (9), 1825-1830.

(7) Tanner, R.L.; Parkhurst, W.J.; Valente, M.L.; David Phillips, W., Regional composition of PM_{2.5} aerosols measured at urban, rural and “background” sites in the Tennessee valley. *Atmos. Environ.* **2004**, *38* (20), 3143-3153.

(8) Turpin, B.J.; Lim, H.-J., Species Contributions to PM_{2.5} Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass. *Aerosol Sci. Technol.* **2001**, *35* (1), 602-610.

Table S1. Accurate mass fittings for measured ions in ESI positive ion mode from chamber experiments with acidified MgSO₄ seed under dry conditions for retention times of 5-8 and 9-14 min.

Measured <i>m/z</i>	Ion	Proposed formula	Theoretical <i>m/z</i>	Diff (mDa)	DBE
Retention time: 5 – 8 min					
137.08072	(M+H)+	C ₅ H ₁₂ O ₄	137.08084	0.12	0
237.13316	(M+H)+	C ₁₀ H ₂₀ O ₆	237.13326	0.11	1
255.14415	(M+H)+	C ₁₀ H ₂₂ O ₇	255.14383	-0.32	0
259.11587	(M+Na)+	C ₁₀ H ₂₀ O ₆	259.11521	-0.66	1
277.12636	(M+Na)+	C ₁₀ H ₂₂ O ₇	277.12577	-0.59	0
355.19653	(M+H)+	C ₁₅ H ₃₀ O ₉	355.19626	-0.27	1
359.16765	(M+Na)+	C ₁₅ H ₂₈ O ₈	359.16764	-0.01	2
373.20717	(M+H)+	C ₁₅ H ₃₂ O ₁₀	373.20682	-0.35	0
377.17919	(M+Na)+	C ₁₅ H ₃₀ O ₉	377.1782	-0.98	1
395.18987	(M+Na)+	C ₁₅ H ₃₂ O ₁₀	395.18877	-1.10	0
473.25933	(M+H)+	C ₂₀ H ₄₀ O ₁₂	473.25925	-0.06	1
477.23059	(M+Na)+	C ₂₀ H ₃₈ O ₁₁	477.23063	0.05	2
491.27000	(M+H)+	C ₂₀ H ₄₂ O ₁₃	491.26982	-0.17	0
495.24214	(M+Na)+	C ₂₀ H ₄₀ O ₁₂	495.2412	-0.93	1
513.25261	(M+Na)+	C ₂₀ H ₄₂ O ₁₃	513.25176	-0.84	0
613.30012	(M+Na)+	C ₂₅ H ₅₀ O ₁₅	613.30419	4.08	1
631.31453	(M+Na)+	C ₂₅ H ₅₂ O ₁₆	631.31476	0.24	0
727.39423	(M+H)+	C ₃₀ H ₆₂ O ₁₉	727.39581	1.62	0
731.36577	(M+Na)+	C ₃₀ H ₆₀ O ₁₈	731.36719	1.45	1
749.37624	(M+Na)+	C ₃₀ H ₆₂ O ₁₉	749.37775	1.53	0
Retention time: 9– 14 min					
167.10610	(M+H)+	C ₁₀ H ₁₄ O ₂	167.10666	0.56	4
267.16135	(M+H)+	C ₁₅ H ₂₂ O ₄	267.15909	-2.26	5
347.18495	(M+H)+	C ₂₀ H ₂₆ O ₅	347.18530	0.35	8
365.19608	(M+H)+	C ₂₀ H ₂₈ O ₆	365.19587	-0.21	7
387.17895	(M+Na)+	C ₂₀ H ₂₈ O ₆	387.17781	-1.14	7
451.20949	(M+Na)+	C ₂₅ H ₃₂ O ₆	451.20911	-0.38	10
469.21771	(M+Na)+	C ₂₅ H ₃₄ O ₇	469.21967	1.96	9
487.23083	(M+Na)+	C ₂₅ H ₃₆ O ₈	487.23024	-0.59	8
505.24069	(M+Na)+	C ₂₅ H ₃₈ O ₉	505.24080	0.11	7
547.28908	(M+H)+	C ₃₀ H ₄₂ O ₉	547.29016	1.08	10
569.27281	(M+Na)+	C ₃₀ H ₄₂ O ₉	569.27210	-0.71	10
647.34255	(M+H)+	C ₃₅ H ₅₀ O ₁₁	647.34259	0.04	11
669.32510	(M+Na)+	C ₃₅ H ₅₀ O ₁₁	669.32453	-0.57	11
733.35478	(M+Na)+	C ₄₀ H ₅₄ O ₁₁	733.35583	1.05	14
751.36618	(M+Na)+	C ₄₀ H ₅₆ O ₁₂	751.36640	0.22	13

769.37637	(M+Na)+	C ₄₀ H ₅₈ O ₁₃	769.37696	0.59	12
833.40590	(M+Na)+	C ₄₅ H ₆₂ O ₁₃	833.40826	2.36	15
851.41803	(M+Na)+	C ₄₅ H ₆₄ O ₁₄	851.41883	0.80	14
933.46009	(M+Na)+	C ₅₀ H ₇₀ O ₁₅	933.46059	0.50	16
951.46835	(M+Na)+	C ₅₀ H ₇₂ O ₁₆	951.47126	2.91	15

110

111 **Table S2.** Detection of IEPOX-derived oligomeric species with high degree of unsaturation from
 112 field samples collected at Centerville, AL (06/15/2013), Look Rock, TN (06/15/2013), and
 113 Yorkville, GA (07/04/2010).

Proposed formula	DBE	Ion	Measured m/z	Theoretical m/z	Diff (mDa)	Field Site
C ₁₀ H ₁₄ O ₂	4	(M+H)+	167.10650	167.10666	0.19	Centerville, AL
		(M+H)+	167.10660	167.10666	0.04	Look Rock, TN
		(M+H)+	167.10585	167.10666	0.80	Yorkville, GA
C ₁₅ H ₂₂ O ₄	5	(M+H)+	267.15870	267.15909	0.40	Centerville, AL
		(M+H)+	267.15910	267.15909	0.17	Look Rock, TN
		(M+NH ₄)+	284.18261	284.18563	-0.58	Yorkville, GA
C ₂₀ H ₂₆ O ₅	8	(M+Na)+	369.16899	369.16725	-1.75	Yorkville, GA
C ₂₀ H ₂₈ O ₆	7	(M+NH ₄)+	382.22140	382.22240	0.99	Centerville, AL
		(M+Na)+	387.18110	387.17781	-0.99	Look Rock, TN
		(M+Na)+	387.17684	387.17787	0.97	Yorkville, GA
C ₂₅ H ₃₂ O ₆	10	(M+H)+	429.22770	429.22720	-0.49	Look Rock, TN
		(M+Na)+	451.20848	451.20911	0.60	Yorkville, GA
C ₂₅ H ₃₆ O ₈	8	(M+NH ₄)+	482.27433	482.27484	0.51	Yorkville, GA
C ₂₅ H ₃₈ O ₉	7	(M+H)+[-H ₂ O]	465.25080	465.24830	0.79	Centerville, AL
C ₃₀ H ₄₂ O ₉	10	(M+Na)+	569.27442	569.27210	-2.32	Yorkville, GA
C ₃₅ H ₅₀ O ₁₁	11	(M+H)+	647.34639	647.34259	-3.80	Yorkville, GA
		(M+Na)+	669.32387	669.32453	1.20	Yorkville, GA
C ₄₀ H ₅₄ O ₁₁	14	(M+NH ₄)+[-H ₂ O]	710.38990	733.39060	-0.75	Centerville, AL
		(M+NH ₄)+[-H ₂ O]	710.39330	733.39060	1.15	Look Rock, TN
		(M+NH ₄)+	728.40333	728.40044	-2.89	Yorkville, GA
C ₄₀ H ₅₆ O ₁₂	13	(M+Na)+	751.36939	751.36640	-2.99	Yorkville, GA
C ₄₀ H ₅₈ O ₁₃	12	(M+NH ₄)+[-H ₂ O]	746.40870	746.41100	2.26	Look Rock, TN
C ₄₅ H ₆₂ O ₁₃	15	(M+Na)+[-H ₂ O]	815.39846	815.39770	-0.76	Yorkville, GA
C ₄₅ H ₆₄ O ₁₄	14	(M+Na)+	851.42054	851.41883	-1.71	Yorkville, GA
C ₅₀ H ₇₀ O ₁₅	16	(M+NH ₄)+	928.50182	925.50530	3.48	Yorkville, GA

114

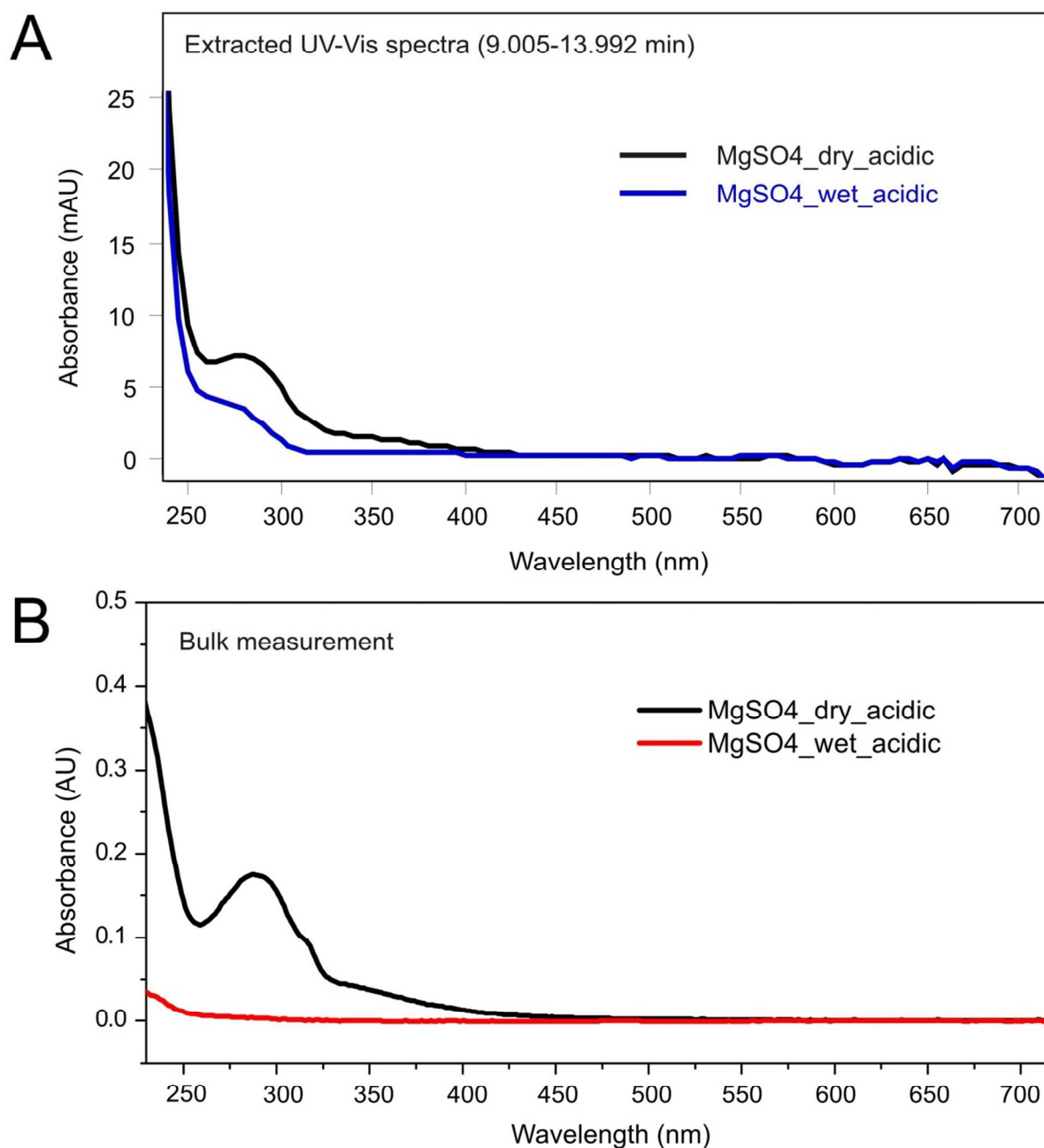


Fig. S1. UV-Vis spectra from (A) UPLC/DAD of SOA constituents eluted at 9-14 minutes in the chromatographic run and (B) bulk measurements of chamber aerosol samples. The SOA constituents eluting between 9-14 min explain most of the light-absorption from the bulk measurements.

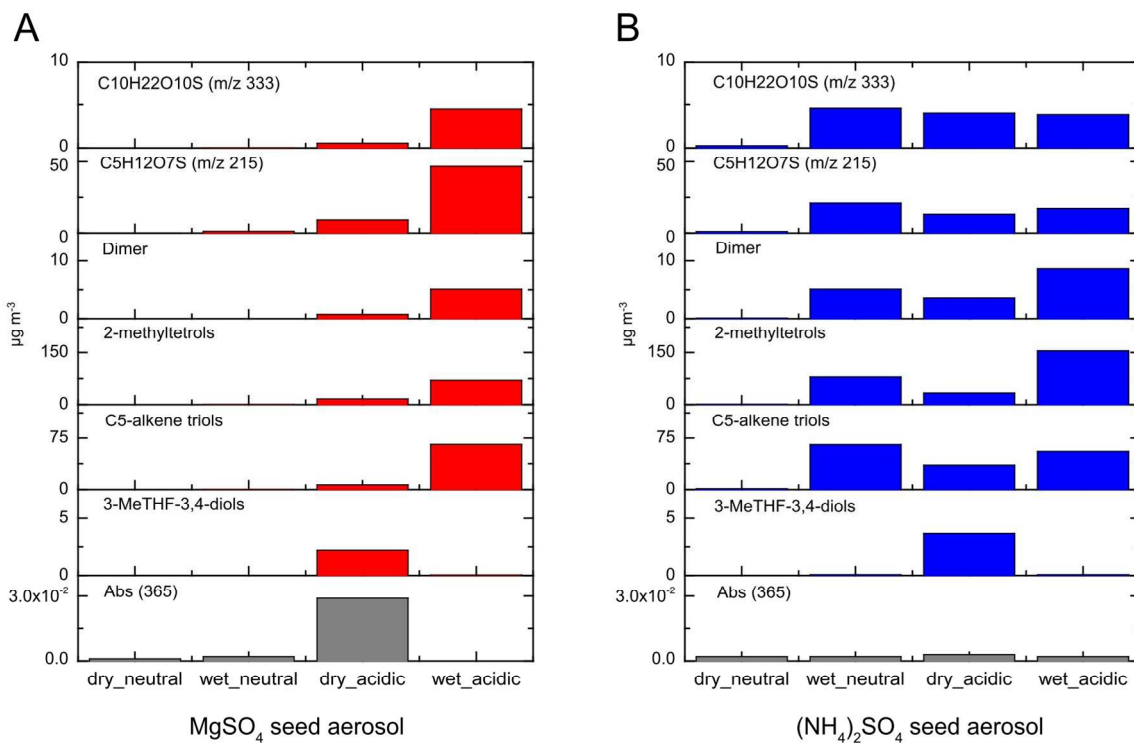


Fig. S2. Comparisons of the light absorbance at 365 nm (AU) and characterized SOA tracer mass concentrations ($\mu\text{g m}^{-3}$) from the following: (a) MgSO_4 system and (b) $(\text{NH}_4)_2\text{SO}_4$ system.

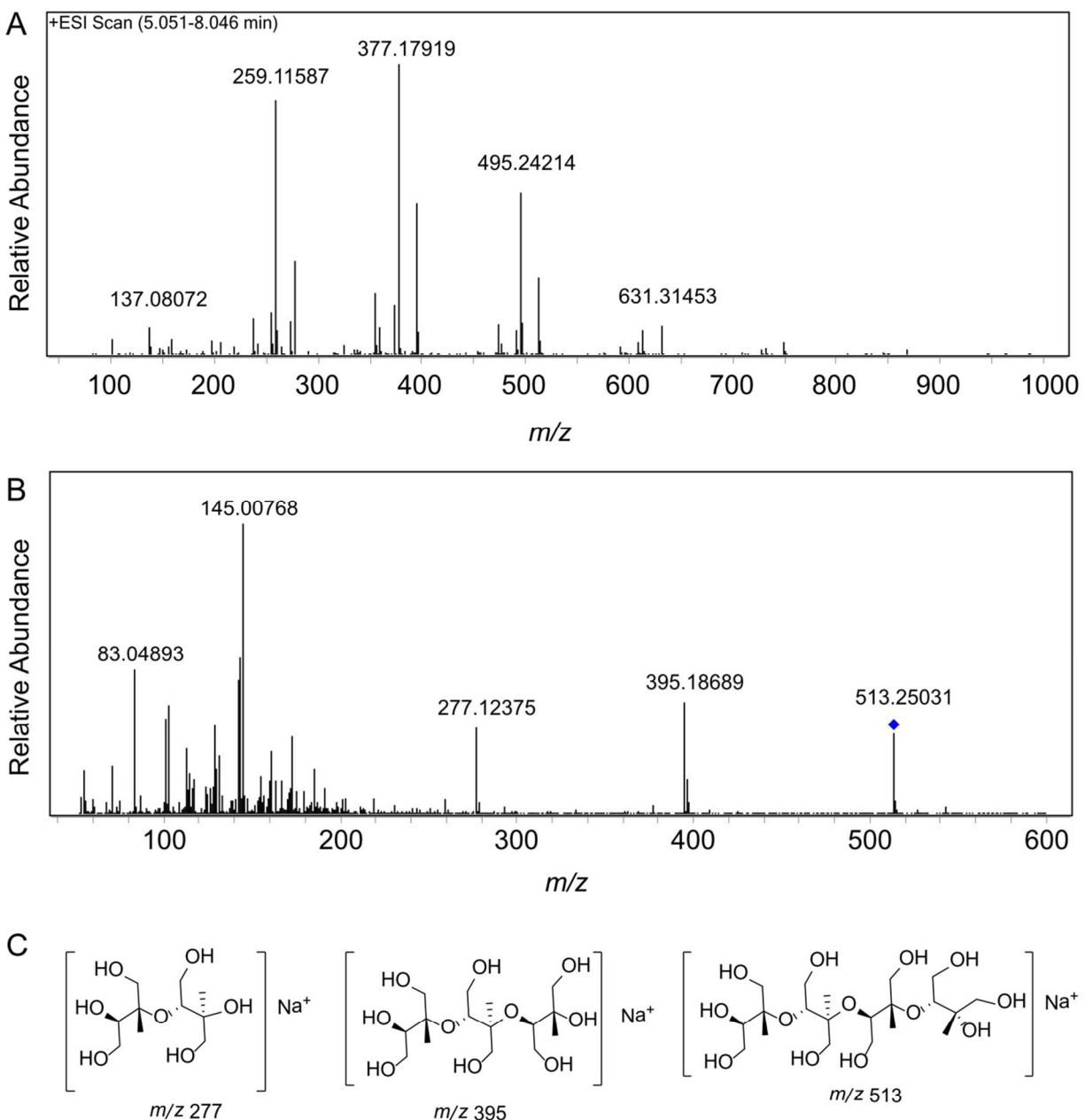


Fig. S3. (A) Full-scan mass spectra of oligomers eluted between 5 and 8 min. (B) MS² spectrum of precursor ion m/z 513 (0 DBE oligomer). (C) Proposed structures for major product ions obtained from collision-induced dissociation of m/z 513 in UPLC/DAD-ESI-HR-QTOFMS (fragmentor voltage: 100 V; collision energy: 60 eV). Proposed structures of product ions agree with elemental compositions obtained from accurate mass fittings within ± 2 mDa.

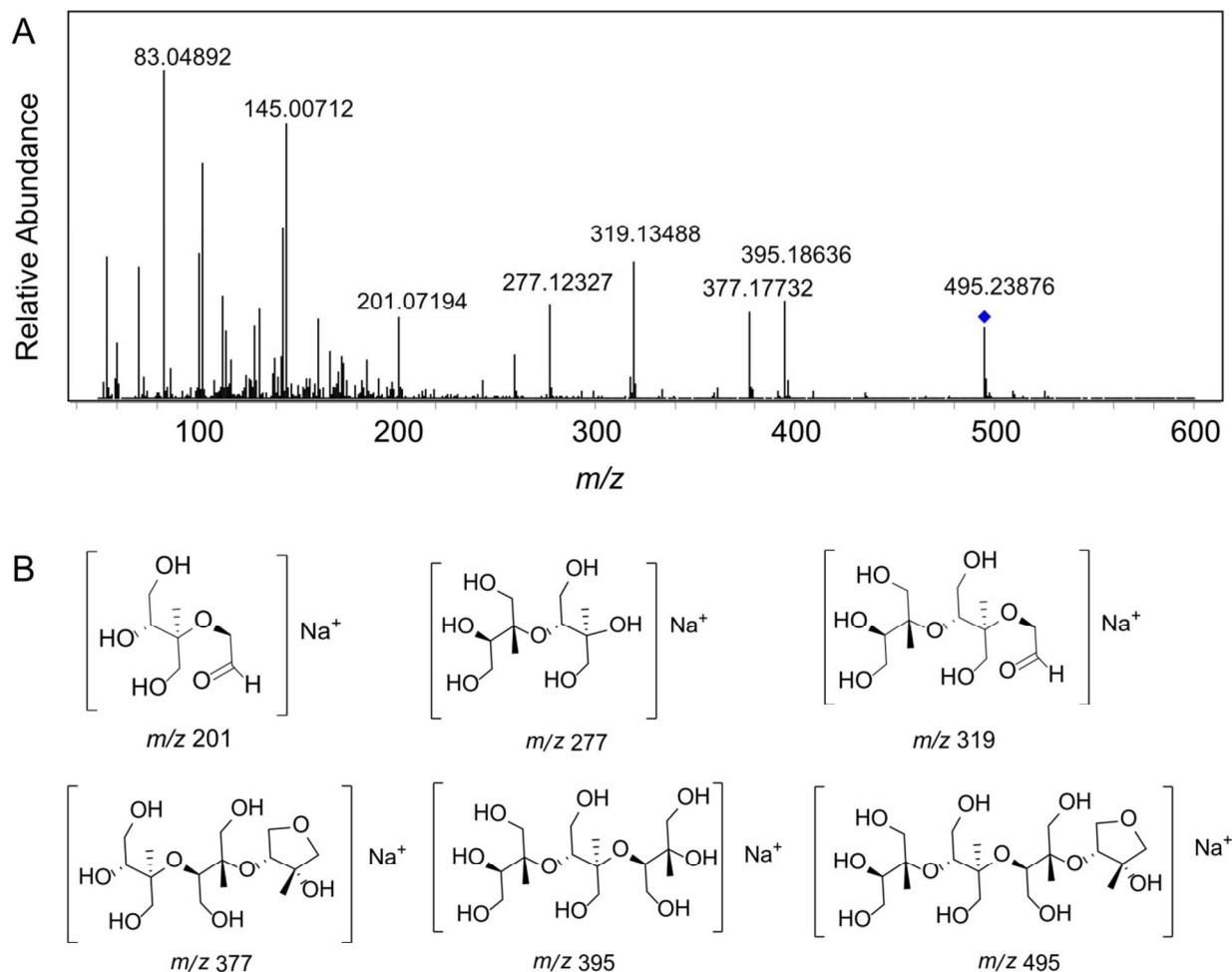


Fig. S4. (A) MS² spectrum of precursor ion m/z 495 (1 DBE oligomer). (B) Proposed structures for major product ions obtained from collision-induced dissociation of m/z 495 in UPLC/DAD-ESI-HR-QTOFMS (fragmentor voltage: 100 V; collision energy: 60 eV). Proposed structures of product ions agree with elemental compositions obtained from accurate mass fittings within ± 2 mDa.

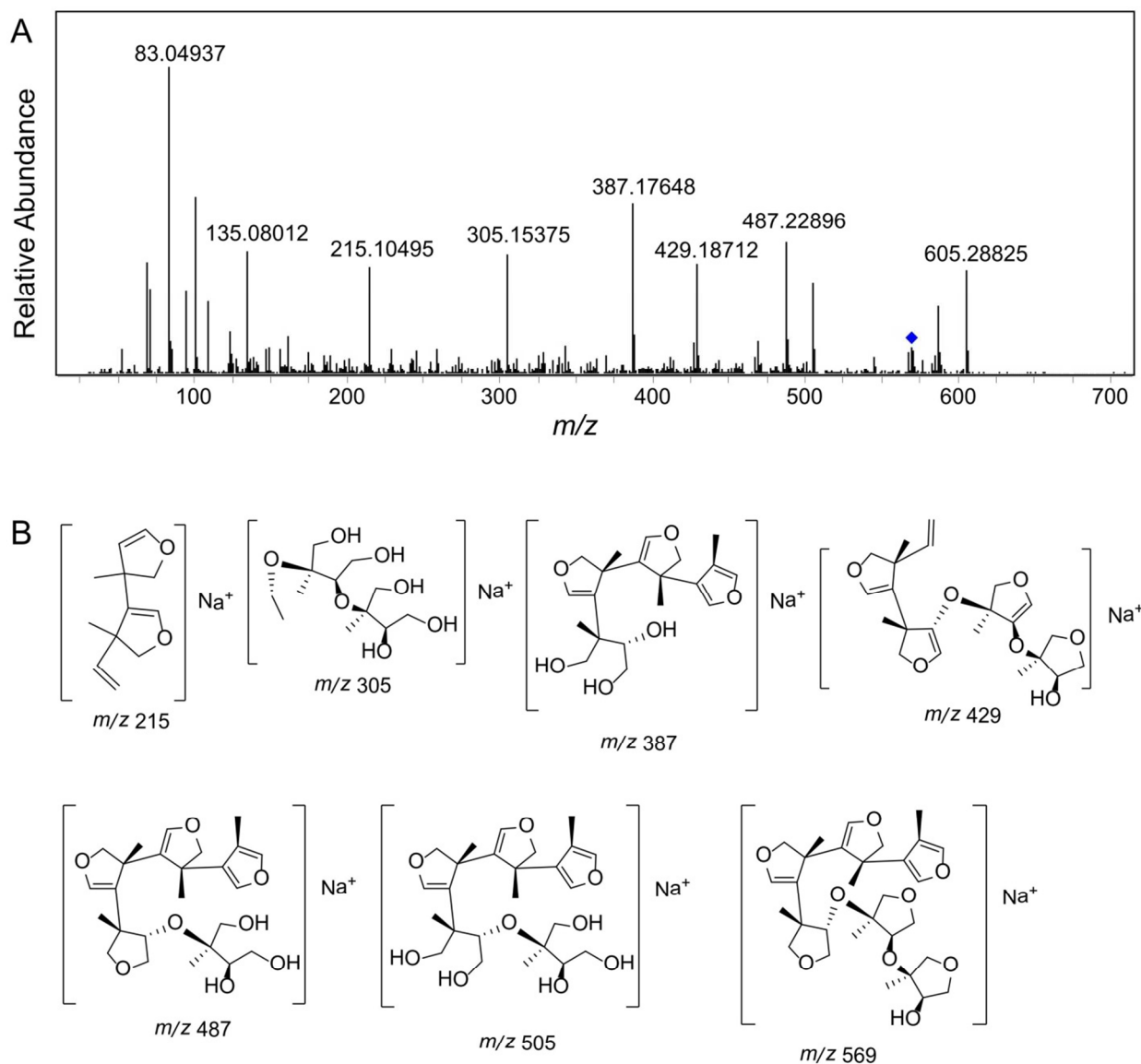
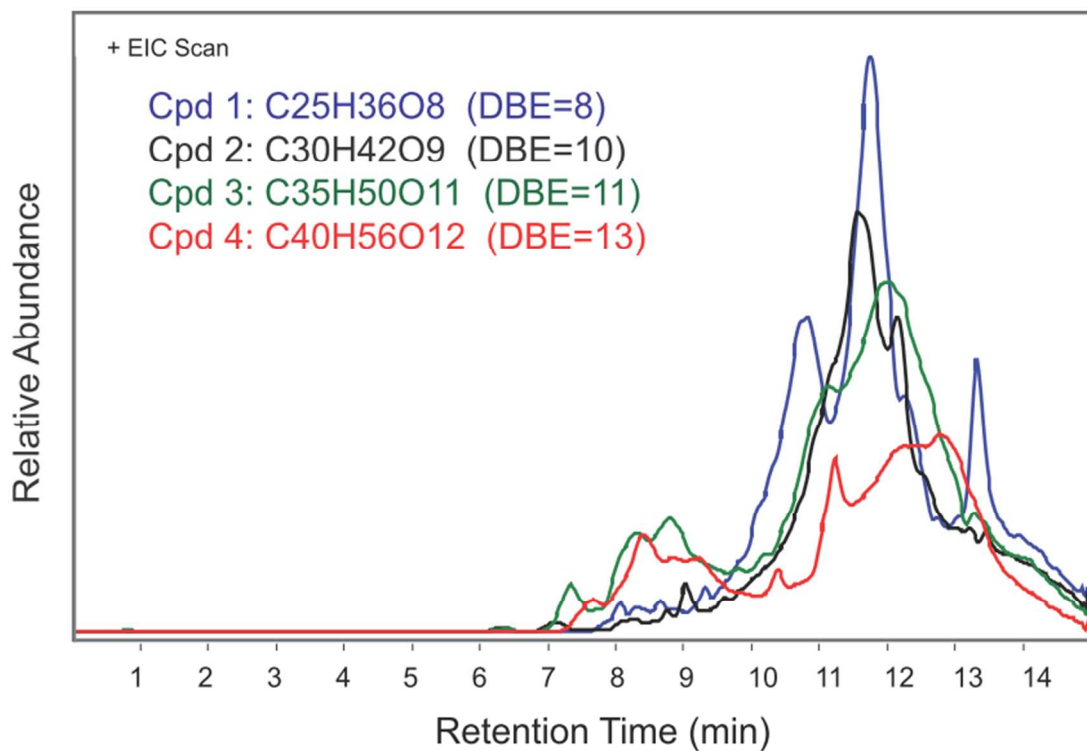


Fig. S5. (A) MS² spectrum of precursor ion m/z 569 (10 DBE oligomer). (B) Proposed structures for major product ions obtained from collision-induced dissociation of m/z 569 in UPLC/DAD-ESI-HR-QTOFMS (fragmentor voltage: 100 V; collision energy: 60 eV). Proposed structures of product ions agree with elemental compositions obtained from accurate mass fittings within ± 2 mDa.



142
143 **Fig. S6.** Extracted ion chromatograms (electrospray ionization; positive ion mode) of identified
144 oligomer series in chamber-generated aerosol samples.