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Light-Absorbing Oligomer Formation in Secondary Organic Aerosol from Reactive Uptake of Isoprene Epoxydiols

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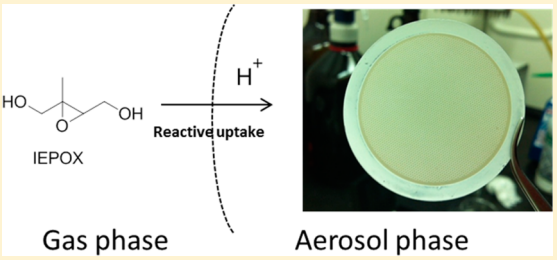
Supporting Information

ABSTRACT: Secondary organic aerosol (SOA) produced from reactive uptake and multiphase chemistry of isoprene epoxydiols (IEPOX) has been found to contribute substantially (upward of 33%) to the fine organic aerosol mass over the Southeastern U.S. Brown carbon (BrC) in rural areas of this region has been linked to secondary sources in the summer when the influence of biomass burning is low. We demonstrate the formation of light-absorbing ($290 < \lambda < 700$ nm) SOA constituents from reactive uptake of *trans*-β-IEPOX onto preexisting sulfate aerosols as a potential source of secondary BrC. IEPOX-derived BrC generated in controlled chamber experiments under dry, acidic conditions has an average mass absorption coefficient of ~300 $cm^2\ g^{-1}$. Chemical analyses of SOA constituents using UV−visible spectroscopy and high-resolution mass spectrometry indicate the presence of highly unsaturated oligomeric species with molecular weights separated by mass units of 100 ($C_5H_8O_2$) and 82 (C_5H_6O) coincident with the observations of enhanced light absorption, suggesting such oligomers as chromophores, and potentially explaining one source of humic-like substances (HULIS) ubiquitously present in atmospheric aerosol. Similar light-absorbing oligomers were identified in fine aerosol collected in the rural Southeastern U.S., supporting their atmospheric relevance and revealing a previously unrecognized source of oligomers derived from isoprene that contributes to ambient fine aerosol mass.



INTRODUCTION

Atmospheric fine aerosol significantly impacts Earth's climate directly through scattering and absorbing solar radiation and indirectly through aerosol−cloud interactions.[1] The combined effects of atmospheric aerosol on total radiative forcing (RF) constitute a major source of uncertainty in climate models, with the consequence that confidence in assessments of the effects on climate change is lacking.[2] Secondary organic aerosol (SOA) produced by atmospheric transformation of gaseous hydrocarbon precursors is generally not considered as a source of light-absorbing materials and is therefore not well-represented in current climate models. However, recent laboratory and field observations indicate SOA composed of either humic-like substances (HULIS) or nitrogen-containing species derived from anthropogenic and biogenic sources have significant light absorbance in the near-ultraviolet (UV) and visible range associated with brown carbon (BrC).[3−6] Such observations establish the need to better identify and quantify sources of light-absorbing SOA and suggest that the warming contribution of organic carbonaceous aerosol is likely to be underestimated in models which do not incorporate a realistic treatment of this potentially important source of positive RF.

Recent investigations of the atmospheric transformations of isoprene (2-methyl-1,3-butadiene) emissions from terrestrial vegetation have demonstrated the importance of relative humidity (RH) as well as anthropogenically mitigated levels of oxides of nitrogen (NO_x) and aerosol acidity in isoprene SOA formation.[7,8] Substantial isoprene SOA (upward of 33% of the organic mass fraction in fine aerosol) has been observed in recent field studies in the Southeastern U.S. where biogenic SOA formation is enhanced by anthropogenic influences.[9,10] During summer, when emissions from biomass burning are low in the rural southeast,[11,12] secondary BrC from biogenic sources was suggested to contribute a major fraction of soluble BrC.[12,13] Nevertheless, light-absorbing properties of SOA from isoprene photooxidation products and the extent to which isoprene-derived SOA might contribute to BrC aerosol have not been considered to date in evaluating the environmental impact of atmospheric BrC.

We report here that SOA derived from the reactive uptake of isoprene epoxydiols (IEPOX), second-generation photochemical oxidation products of isoprene under low-NO_x conditions, onto acidified sulfate seed aerosol yields SOA with a chemical composition similar to HULIS and may be a substantial contributor to the absorbance of tropospheric UV and visible

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Table 1. Summary of Experimental Conditions

seed type	acidity		RH (%)[a]	aerosol mass conc. (μg m^{-3})[b]	organic mass conc. (μg m^{-3})[c,d]	⟨MAC⟩ (cm^2 g^{-1})[d,e]
$MgSO_4$	neutral	dry	6.1	26.5		
		wet	58.6	32.5		
	acidified	dry	8.6	66.6	29.6	344
		wet	51.1	94.2	42.3	11
$(NH_4)_2SO_4$	neutral	dry	6.9	42.5		
		wet	48.9	84.9	43.4	15
	acidified	dry	5.5	169.2	117.1	8
		wet	58.5	110.8	68.9	13

[a]Chamber conditions before injection of *trans*-β-IEPOX. Temperatures ranged between 24 and 25 °C. [b]Aerosol mass concentrations estimated from measured volume concentrations and averaged over the course of filter sampling, with the aerosol density assumed to be 1.25 g cm^{-3}. [c]Estimated organic mass concentrations during filter collection. [d]Blanks indicate that there was no observable signals with our methods. [e]Averaged MAC over 290−700 nm.

solar radiation (290−700 nm). The absorbance measured from the filter extracts of aerosol samples generated in chamber experiments is correlated with the presence of oligomers. Molecular composition and mass fragmentation patterns show that the oligomers are composed of highly oxygenated monomeric units derived from the C_5 isoprene skeleton. Our chamber studies demonstrate that molecular composition is dependent on aerosol pH and suggest that light-absorbing structures are generated via successive dehydrations under conditions of enhanced acidity. Fourier transform infrared (FTIR) analysis of the total SOA extract from our chamber studies indicates that carbonyl compounds are not major SOA components and taken together with the mass spectra of the oligomers, is not supportive of carbonyl groups as significant chromophores. This observation stands in contrast to previously reported laboratory studies on the formation of BrC, which are based on acid-catalyzed coupling of semivolatile carbonyl precursors[6,14−22] or alkenes[23] where browning is attributed to formation of SOA products similar to those of Maillard reactions or polyconjugated systems. Confirmation of both the spectral characteristics of the aerosol sample extracts and the presence of the same oligomers in chamber samples and field samples collected from the Southeastern U.S. indicates that the chamber studies reproduce an environmentally relevant process. Given that isoprene is the most abundant nonmethane hydrocarbon emitted into the atmosphere (∼600 Tg y^{-1}),[24] our study points to IEPOX as a hitherto unrecognized source of BrC in isoprene-rich regions. Our results also yield insights into the molecular-level characterization and quantification of BrC constituents that have the potential to improve the accuracy of calculating RFs that determine the overall radiative balance.

■ EXPERIMENTAL SECTION

Chamber Experiments. Reactive uptake experiments were performed in a 10-m^3 flexible Teflon indoor chamber at the University of North Carolina. The chamber has been described in detail previously.[25] Prior to each experiment the chamber was flushed for at least 24 h until particle number concentrations were below 15 cm^{-3}, and volume concentrations were ∼10^{-3} μm^3 cm^{-3}. Particle number concentrations, size distributions, and volume concentrations were continuously monitored using a differential mobility analyzer (DMA, BMI model 2002) coupled to a mixing condensation particle counter (MCPC, BMI model 1710). Two types of sulfate seed aerosol were used to promote reactive uptake of organic material: $MgSO_4$ (0.06 M) and $(NH_4)_2SO_4$ (0.06 M). Acidified sulfate seed aerosol was generated by adding additional sulfuric acid (0.06 M) to seed aerosol solutions. Seed aerosol was atomized into the chamber using a home-built nebulizer at a flow rate of 4 L min^{-1} until a total aerosol volume concentration of 30 μm^3 cm^{-3} was attained. Experiments were conducted under wet (∼50% RH) or dry (<10% RH) conditions. Temperature and RH inside the chamber were monitored using an OM-62 temperature relative humidity data logger (OMEGA Engineering, Inc.). A summary of typical experimental conditions is given in Table 1. Experiments were repeated multiple times with similar results.

Trans-β-IEPOX (15 mg) was synthesized by a published procedure[26] and introduced into the chamber by passing high-purity N_2 gas at 2 L min^{-1} through a manifold heated to ∼70 °C for 4 h. Following 4 h of reaction, SOA stabilized and aerosol samples were collected onto Teflon membrane filters (47 mm diameter, 1.0 μm pore size; Pall Life Science) at a flow rate of 25 L min^{-1} for 2 h. Exact mass loadings on the filters were determined based on calculations of total volume sampled multiplied by the average mass concentrations of aerosols during the sampling period, and assuming a density of 1.25 g cm^{-3} for IEPOX-derived SOA (i.e., isoprene low-NO_x SOA) to convert measured volume concentrations to mass concentrations.[27] Following collection, filter samples were stored in 20 mL scintillation vials at −20 °C until analysis. Filters were extracted with methanol, and subsequently analyzed by optical and chemical measurements to examine the light-absorption properties and molecular features of resultant SOA constituents.

Collection of aerosol samples onto filters with subsequent off-line optical and chemical analyses is currently state-of-the-art for characterizing aerosol composition, since online optical instruments, such as the photoacoustic extinctiometer (PAX) or cavity ring-down/photoacoustic spectrometer (CRD-PAS), cannot provide detailed chemical characterization of the light-absorbing aerosol components at the molecular level. In addition, these online techniques are also limited in the available wavelength response owing to the implementation of discrete light sources. In order to determine the full absorption properties from these measurements, it is necessary to calculate the wavelength-dependence described using band gap theory[28] or by calculating absorption Ångström exponents,[29−31] whereas UV−vis measurements directly measure the entire absorption region of interest without the need for further assumptions. As discussed in the Supporting Information, artifacts arising from filter collection, post-collection storage and extraction processes

on SOA characteristics are unlikely to have affected the results of this study.

UV−visible Spectroscopy. Filter samples were extracted in 20 mL of high-purity methanol (LC-MS Chromasolv, Sigma-Aldrich) and sonicated for 45 min. Filter extracts were blown dry with a gentle nitrogen stream, reconstituted in 1 mL methanol, and transferred to a 1 cm path length quartz cuvette. UV−vis spectra were acquired on a Hitachi U-3300 dual beam spectrophotometer, scanning from 290 to 700 nm (at 300 nm min^{-1}) with methanol as reference. Extracts from seed aerosol-only and blank Teflon filters were analyzed as controls.

UPLC/DAD-ESI-HR-QTOFMS. Chromatographic separation, optical detection, and mass spectral data were acquired by ultra-performance liquid chromatography (UPLC) coupled in-line to both a diode array detector (DAD) and high-resolution quadrupole time-of-flight mass spectrometer equipped with an electrospray ionization source (ESI-HR-QTOFMS, Agilent 6500 Series). Deatiled operating parameters for UPLC and ESI-HR-QTOFMS have been published.[32] Sample aliquots (5 μL) were injected into the in-line DAD scanning over a 200−800 nm range (5 nm steps), and the effluent was directed into the ionization source of the mass spectrometer. Sodium propyl sulfate (electronic grade, City Chemical LLC) was used as a surrogate standard to quantify IEPOX-derived organosulfates.

Gas Chromatography/Mass Spectrometry (GC/MS). Aliquots (200 μL) of extracts used to acquire UV−vis spectra were blown dry on a nitrogen evaporator at room temperature. The residues were derivatized with 100 μL of BSTFA + TMCS (99:1 v/v, Supelco) and 50 μL of pyridine (anhydrous, 99.8%, Sigma-Aldrich), heated at 70 °C for 1 h prior to GC/MS analysis. For analysis, 1 μL aliquots were injected onto an Econo-Cap-EC-5 Capillary Column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) in a Hewlett-Packard (HP) 5890 Series II Gas Chromatograph coupled to a HP 5971A Mass Selective Detector. Operating conditions have been described previously.[8] Then, *cis*- and *trans*-3-MeTHF-3,4-diols, as well as 2-methyltetrols, were quantified with authentic standards. The 2-methyltetrols served as surrogate standards for quantification of the C_5-alkene triols.

Fourier Transform Infrared Spectroscopy (FTIR). The ATR-FTIR spectra were recorded on a Thermoscientific FTIR Spectrometer (Nicolet iS10, ∼20 bounce) equipped with a Spectratech ATR with liquid trough accessory. Filters were extracted in 20 mL of methanol and concentrated to ∼100 μL under a gentle stream of N_2. The concentrate was spotted onto the ATR crystal and dried. The ATR-FTIR spectra were acquired by averaging 512 scans with 4 cm^{-1} resolution over 4000−700 cm^{-1}. Background correction was acquired using methanol extracts of clean filters. A control spectrum of 100 μL pure methanol dried onto the ATR crystal showed negligible intensity in the 300−3400 cm^{-1} region, ruling out solvent interferences.

Analysis of Ambient Fine Aerosol Samples. Ambient $PM_{2.5}$ samples collected from the rural Southeastern U.S., including Yorkville, GA, during the summer of 2010, and Look Rock, TN, and Centreville, AL, during the 2013 Southern Oxidant and Aerosol Study (SOAS), were analyzed to examine the atmospheric relevance of our chamber findings. A detailed description of the Yorkville site, collocated measurements, and procedure for aerosol sample analyses by UPLC/DAD-ESI-QTOFMS is given elsewhere.[9] A detailed description of field sites and $PM_{2.5}$ sampling during the 2013 SOAS campaign is provided in Supporting Information.

■ RESULTS AND DISCUSSION

Light-absorbing material from isoprene oxidation products was first reported in a laboratory study in which SOA generated by dark ozonolysis of high concentrations of isoprene appeared light brown in color,[33] but the investigators did not further probe the source of the absorbance. Subsequently, the formation of light-absorbing material in aerosol has been examined by numerous laboratories with the specific objective of elucidating potential chromophores and reaction pathways. The focus of much of this research has been on dark reactions of semivolatile carbonyls, particularly glyoxal and methylglyoxal, in the presence of ammonia, ammonium ion, or other nitrogen-containing compounds under a variety of conditions, and demonstrated chromophores having C−N bonds.[14−20] Oxidation of a number of biogenic volatile organic compounds with hydroxyl (OH) radicals or ozone and subsequent exposure of the resulting SOA to ammonia yielded light-absorbing products, although absorbance was not observed in the case of isoprene SOA under these experimental conditions.[34] Aldol condensation of carbonyl-containing precursors[6,22] and acid-catalyzed oligomerization of alkenes, including isoprene and terpenes,[35] have also been investigated as a sources of light-absorbing aerosols not containing C−N linkages. The results of the laboratory and chamber investigations have been uniformly interpreted as suggestive that the precursors investigated were potential sources of atmospheric BrC, but confirmation of the relevance of experimental conditions to those in which BrC has been observed in field studies and the structures of the compounds proposed as light-absorbing species is lacking.

Identification of IEPOX isomers as major second-generation photooxidation products of isoprene prompted our chamber studies to test the hypothesis that oligomers from acid-catalyzed reactive uptake of IEPOX might be processed to yield chromophores under conditions of strong acidity and high ionic activity at aerosol surfaces present under tropospheric conditions. Table 1 summarizes chamber conditions and the results of the reactive uptake of IEPOX investigated in this work.

Experimental Conditions Yielding Light-Absorbing SOA Extracts. Absorbance of SOA extracts can be described by the wavelength-dependent effective mass absorption coefficient (MAC, $cm^2\ g^{-1}$)[34,36] according to eq 1.

$$\mathrm{MAC}(\lambda) = \frac{A_{10}(\lambda)\times \ln 10}{b \times C_{\mathrm{mass}}} \tag{1}$$

where $A_{10}(\lambda)$ is $\log_{10}$ absorbance at wavelength (λ) of SOA extracts in solution, b is path length (cm), and C_{mass} ($g\ cm^{-3}$) is the solution mass concentration of material from the heterogeneous reactive uptake of IEPOX onto seed aerosol. C_{mass} is derived from the difference between the measured total aerosol mass concentration and the contribution of inorganic seed aerosol. Measured concentrations are wall-loss uncorrected for direct comparison of measured optical properties under different experimental conditions. The light-absorbing properties of IEPOX-derived SOA extracts obtained in the experiments listed in Table 1 can be compared by MAC averaged over the wavelengths associated with natural sunlight (290−700 nm) determined by eq 2.

$$\left\langle \mathrm{MAC} \right\rangle = \frac{1}{(700 - 290)\ \mathrm{nm}} \times \int_{290\mathrm{nm}}^{700\mathrm{nm}} \mathrm{MAC}(\lambda)\ \mathrm{d}\lambda \quad (2)$$

Lambe et al.[37] performed experiments to compare the difference between MAC values assessed with online cavity ring-down spectrometry coupled with photoacoustic spectrometry (CRDS-PAS) and those obtained with UV−vis measurements of filter extracts. The authors concluded that there is generally good agreement with MACs differing by 25% or less between techniques. In many cases, it appears that this difference is within the limits of measurement error, indicating that the extraction processes does not appreciably alter the aerosol optical properties.

Notably, aerosol samples collected from IEPOX uptake onto dry acidified $MgSO_4$ seed were visibly brown in color (as shown in TOC Art). The MAC of filter extracts had a strong absorbance maximum at ∼300 nm with a broad, partly resolved shoulder at ∼340 nm tailing toward 500 nm in the visible region (Figure 1). The ⟨MAC⟩ was 30-fold higher (Table 1) than that obtained from acidified $MgSO_4$ seed aerosol under conditions of higher RH; however, traces of extracts from the higher RH experiments were qualitatively similar, suggesting the presence of similar chromophores at greatly reduced concentration. Under neutral conditions, neither SOA growth nor browning was observed when using $MgSO_4$ seed regardless of RH, indicating that acidity is a key factor leading to browning. The magnitude of browning shown in Table 1 falls in the range of ⟨MAC⟩ values (50−500 $cm^2\ g^{-1}$) reported previously for isoprene and monoterpene SOA aged in the presence of NH_3 in the absence of aerosol acidity.[34] In the present work, generation of strongly absorbing chromophores derived from IEPOX uptake is not dependent on the presence of nitrogenous compounds or carbonyls. Comparisons of MAC values from field and laboratory studies of organic aerosols reported by Updyke et al. indicate that the measured MACs from IEPOX-derived light-absorbing organic carbon are lower than biomass burning aerosol.[34] However, considering the abundance of IEPOX-derived SOA (upward of 33% of the total organic aerosol mass in the Southeastern U.S. during summer),[10] the impact on regional radiative forcing could still be significant and warrants further investigation.

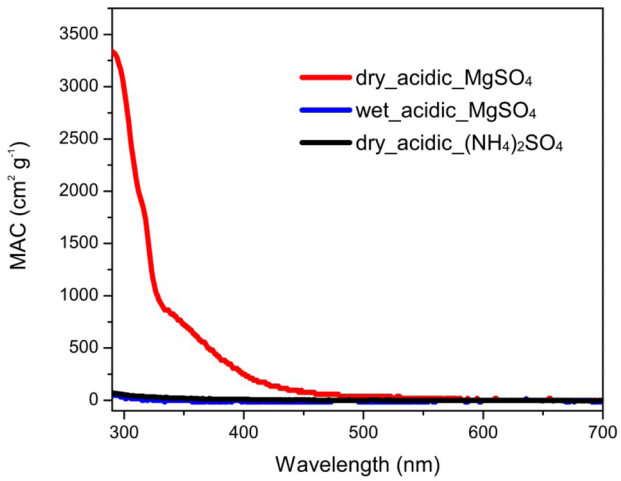

Figure 1. Mass absorption coefficient (MAC) for IEPOX-derived light-absorbing SOA constituents under different experimental conditions.

Only minimal light-absorbing material was observed in experiments with $(NH_4)_2SO_4$ seed aerosol under all conditions, despite the added presence of nitrogen from ammonium sulfate seed. Despite lack of browning, significant SOA growth was observed in experiments at high RH with neutral $(NH_4)_2SO_4$ seed, in contrast to the results with neutral $MgSO_4$ seed under high-RH conditions. These results are consistent with a recent study showing elevated RH conditions facilitate SOA growth from IEPOX uptake by nonacidified $(NH_4)_2SO_4$ seed aerosols.[38] This suggests that higher RH may be associated with higher aerosol liquid water content or change of phase state from solid to liquid-like particles that promotes IEPOX uptake and leads to subsequent SOA formation.[39] Formation of a miscible aerosol liquid phase below the deliquescence RH of 80% by inorganic $(NH_4)_2SO_4$, water, and SOA products from isoprene photooxidation has been reported.[40] However, these results suggest overall that high-RH environments (and thus, reduced aerosol acidity) are not favorable for IEPOX-derived BrC formation.

Aerosol Acidity. Since acidic and low-RH conditions were essential for the production of IEPOX-derived BrC and browning is only observed in the presence of dry acidified $MgSO_4$ seed aerosols but not for the dry acidified $(NH_4)_2SO_4$, aerosol pH was estimated by ISORROPIA II,[41] an aerosol thermodynamic equilibrium model to examine the effect of seed compositions and aerosol acidity. Our results suggested that aerosol acidity is the key parameter leading to this difference. For dry acidified $MgSO_4$ seed aerosol (RH = 8.6%), pH was estimated to be 0.62, whereas for dry acidified $(NH_4)_2SO_4$ seed (RH = 5.5%), a significantly higher pH of 2.25 was estimated. Some uncertainty in the calculation of pH for $(NH_4)_2SO_4$ seed using ISORROPIA II arises from the extensive formation of organosulfates on reactive uptake of IEPOX,[42] which depletes the concentration of free inorganic sulfate and causes charge imbalance. However, our pH estimates for both acidified seed types are similar to those of Gao et al.[43] and clearly establish that the formation of light-absorbing constituents from IEPOX on the acidified $MgSO_4$ seed was catalyzed by a substantial decrease in pH relative to the acidified $(NH_4)_2SO_4$ seed. Importantly, the observations of low aerosol pH in ambient $PM_{2.5}$ have been reported in several studies.[44,45] Evaporation of aerosol droplets in the atmosphere as a consequence of decreasing relative humidity (RH) is known to provide a highly concentrated and supersaturated microenvironment within the shrinking droplets that shifts chemical equilibria.[15,17,36]

Additionally, $MgSO_4$ aerosols have been reported to form a gel-like chain structure of contact ion pairs at low-RH conditions.[15,16] We suspect that the formation of such chain structures limits the mass transfer (and thus uptake) of IEPOX and influences the phase state of seed aerosols. The possible involvement of Mg^{2+} chemistry is discussed in the Supporting Information.

Molecular Composition of IEPOX-Derived BrC. Figure 2 compares the traces of (A) optical density at 365 nm, (B) negative ion total ion chromatogram (TIC), and (C) positive ion TIC from analysis of filter extracts of SOA collected in the experiment with dry acidified $MgSO_4$ seed, the only conditions leading to visible browning. The analysis was performed by gradient elution reverse-phase UPLC interfaced with a DAD-ESI-HR-QTOFMS. Significant optical density between 10 and 13 min, where less polar components are expected to elute, coincides with significant intensity in the positive TIC trace.

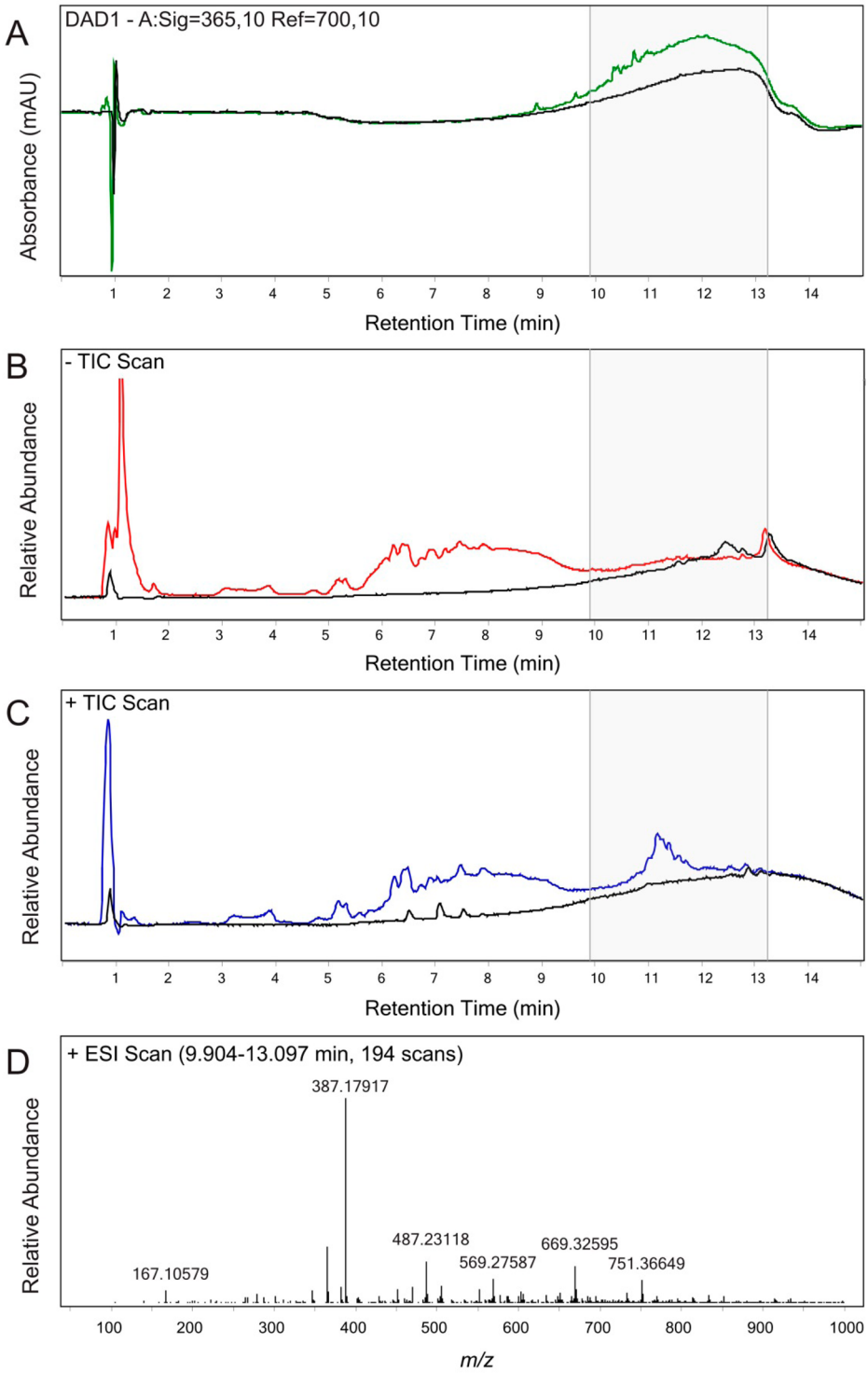

Figure 2. Molecular composition of IEPOX-derived SOA generated under dry acidic conditions with $MgSO_4$ seed aerosol: (A) UPLC diode array detector (DAD) trace at 365 nm with reference at 700 nm; (B) negative ion mode total ion chromatogram (TIC); (C) positive ion mode TIC; and (D) background subtracted mass spectrum corresponding to the positive ion mode TIC for compounds eluting between 10 and 13 min. These traces show that only SOA constituents eluting late in the positive ion mode TIC are associated with light-absorbing properties. Mass spectral data show dehydrated oligomeric products derived from reactive uptake of IEPOX. Mass units between oligomeric ions observed in part D differ by 100 and 82 Da, corresponding to $C_5H_8O_2$ and C_5H_6O. The chemical formulas of detected major ions (protonated or sodiated oligomers) are listed in Table S1. Colored lines: sample from dry acidic experiments with $MgSO_4$ seed. Black lines: blank Teflon filters (no SOA collected).

UV−vis spectra extracted from the DAD trace at retention times greater than 9 min are consistent with UV−vis spectra from bulk measurements (Figure S1) and indicate that the light-absorbing materials represent relatively nonpolar components of the filter extracts. Notably, the absence of artifacts in our filter-based approach to characterization of light-absorbing aerosol components is further supported by the similarity of UV−vis spectra of our bulk filter extracts to the absorption

spectra of ambient aerosol in Athens, GA, acquired by online UV−vis photoacoustic spectrophotometry.[46]

Among the IEPOX-derived SOA tracers characterized by GC/MS and UPLC/DAD-ESI-HR-QTOFMS, including 2-methyltetrols,[47] C_5-alkene triols,[48] dimers,[49] IEPOX-derived organosulfates[8] and isomeric 3-methyltetrahydrofuran-3,4-diols (3-MeTHF-3,4-diols),[25] only 3-MeTHF-3,4-diols were associated with enhanced light absorbance at 365 nm (a surrogate wavelength for BrC absorption)[11] (Figure S2). The acid-catalyzed IEPOX cyclic rearrangement products (3-MeTHF-3,4-diols) were present only under the same dry, acidic conditions which produced the potentially light-absorbing oligomers.

The molecular weights of the major ions in the 10−13 min range are separated by mass units of 100 Da ($C_5H_8O_2$) and 82 Da (C_5H_6O). The compositions in Figure 2D, determined by high-resolution mass measurements, correspond to protonated or sodiated oligomers composed of 5-carbon monomers up to 10 units (Table S1). Multiple oligomers for ions containing identical numbers of C_5-units were distinguished by increasing double bond equivalents (DBEs) accompanied by decreasing water equivalents. DBEs increased from a minimum of 7 in the 4-unit ions to 16 in the 10-unit ions, and overall the oligomers contained high DBEs (i.e., degree of unsaturation) coincident with the absorbance observed at 365 nm. Intensity of the positive ion TIC between 5 and 8 min (Figure 2C) suggests that more polar compounds may account for a significant mass of SOA collected, but do not contribute to optical density. The compositions of the ions eluting during the 5−8 min time frame were also determined by high-resolution mass measurements and found to correspond to oligomers composed of up to six C_5 units containing no more than 2 DBE (Table S1), coincident with the lack of absorbance at 365 nm.

Full-scan mass spectra along with tandem mass spectra (MS^2) of specific ions provide insight into possible structures and pathways of oligomer formation. Between 5 and 8 min, a series of ions having compositions consistent with polyether polyols composed of C_5 units with no DBE are in accord with IEPOX oligomerization. IEPOX dimer ethers as well as larger IEPOX oligomers have been reported previously.[8] Since *trans*-β-IEPOX, which is the predominant IEPOX isomer formed in photochemical oxidation of isoprene,[50] is the monomeric unit in this study, the polymer backbone will consist of two-carbon units (C2−C3 of the 4-carbon isoprene backbone) linked by the ether oxygens, with each backbone carbon having a pendant hydroxymethyl group (Figure 3A). On the strongly acidic catalytic surface of the seed, the pendant hydroxymethyl groups may cyclodehyrate to increase DBE via formation of tetrahydrofuran (THF) rings (Figure 3B). This structure is supported by tandem mass spectra of initially formed polyethers with 0 DBE, which are characterized by loss of 1 C_5 unit (118 Da; $C_5H_{10}O_3$) or 2 C_5 units (236 Da; $C_{10}H_{20}O_6$) as neutral monounsaturated fragments (Figure S3). Tandem mass spectra of polyethers having 1 DBE lose either the cyclic C_5 unit as a dihydrofuran (100 Da; $C_5H_8O_2$) or two C_5 units including the ring (218 Da; $C_{10}H_{18}O_5$) (Figure S4). The molecular composition of less polar ions eluting between 9 and 14 min requires the elimination of a greater number of water equivalents than could be gained by cyclodehydration of pendant hydroxymethyl groups of the initially formed oligomers. We propose that additional DBEs are gained by dehydrative loss of ether oxygens leading to C−C coupled 5-membered rings that could generate structures exemplified in

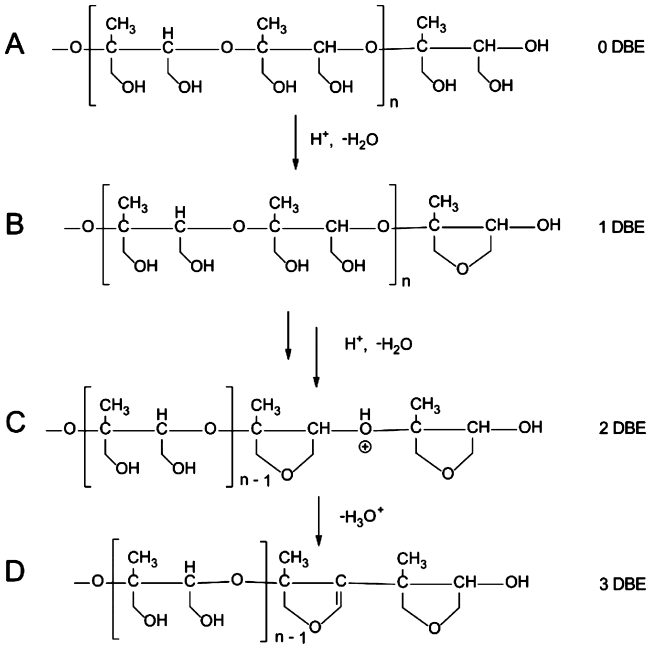

Figure 3. Tentatively proposed evolution of oligomeric species in IEPOX-derived SOA. (A) Initial oligomer derived from H^+ initiated opening of IEPOX oxirane ring; (B) tetrahydrofuran ring formation (1 DBE/ring) by cyclodehydration of pendant hydroxymethylene groups; (C and D) proposed dehydration of ether linkages with formation of dihydrofuran rings (2 DBE/dihydrofuran ring for panel C, 3 DBE total for panel D).

Figure 3C−D. Oligomers observed in filter extracts of SOA collected under low-RH conditions and acidified $MgSO_4$ seed encompass a large range of compositions observed and exact mass measurements along with proposed structures and tandem mass spectra are presented as Supporting Information (Table S1 and Figure S3−S5). The structures in Figure S3−S5 are tentatively proposed as consistent with MS and MS^2 data; however, the broad peaks in chromatographic separations likely reflect a chemically complex mixture containing isomeric chromophores. We also note that more highly unsaturated, less oxygenated oligomers that may be observed in the DAD traces (Figure 2B−C) are generally not efficiently ionized by ESI and may not have been detected in the mass spectrometric analysis. While structures and pathways proposed in this report are considered to be reasonable and consistent with observations, it is to be understood that they are speculative (tentative). However, cyclodehydration with of the 5-membered tetrahydrofuran ring is a highly favorable reaction and has been reported in the synthetic literature for Lewis acids[51] and strong organic acids (*p*-toluenesulfonic acid),[52] trifluoroacetic acid[53] (unspecified pH), at ambient or subambient temperatures. Additional mechanistic discussion can be found in the Supporting Information.

The FTIR spectra of bulk extracts of nonlight absorbing filters illustrated in Figure 4B−C are characterized by strong absorbance at frequencies assigned to alcohol O−H (3300−3500 cm^{-1}) and primary sp^3 C−H stretching modes (<3000 cm^{-1}). There is little intensity attributable to C═O stretching, which would give rise to strong bands at frequencies ∼1700 cm^{-1}. Strong absorbance appears between 950 and 1300 cm^{-1}, where ether C−O—C and alcohol C−OH stretching occurs. The bulk FTIR spectra are thus in overall accord with expectation for mixtures containing the major tracers of reactive

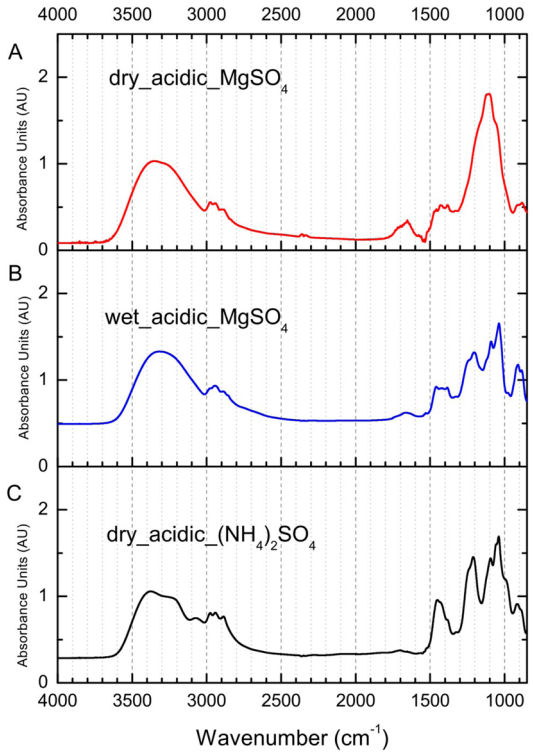

Figure 4. FTIR spectra of bulk IEPOX-derived SOA extracts from filters in experiments with (A) dry acidified $MgSO_4$; (B) wet acidified $MgSO_4$; and (C) dry acidified $(NH_4)_2SO_4$ seed aerosols.

uptake of IEPOX, which include the isomeric 3-MeTHF-3,4-diols, C_5-alkene triols, 2-methyltetrols, and dimer ethers as well as the oligomeric components. In the FTIR spectrum of the bulk extract of the light-absorbing IEPOX-derived SOA, Figure 4A, a broad, intense absorbance centered at ~1150 cm^{-1} replaces multiple bands resolved over the frequency range 975−1350 cm^{-1}. This change is accompanied by growth of intensity in the range 1650−1600 cm^{-1} where C═C stretching is expected. The presence of hydroxy groups, ether bonds, and unsaturation is in accord with UPLC/DAD-ESI-HR-QTOFMS analysis of the extracts of acidified $MgSO_4$ seed aerosol and the structures proposed for the light-absorbing oligomers (Figure 2). The FTIR spectra in Figure 4 are qualitatively similar to the FTIR spectrum reported by Limbeck et al.[23] for the formation of polymeric brown SOA species in filter extracts, consistent with HULIS, generated by the heterogeneous reaction of isoprene with sulfuric acid impregnated on quartz fiber filters.

Detection of Oligomers in Ambient Fine Aerosols. Based on the results of the chamber studies, the presence of the IEPOX-derived light-absorbing oligomers was investigated in ambient $PM_{2.5}$ samples collected at three field sites during summer in the Southeastern U.S. where IEPOX chemistry has been reported to play a major role in the formation of SOA.[9,10] The extracted ion chromatograms (EICs) in Figure 5 confirm the presence of the same oligomers in the field samples (Table S2) that were observed in the chamber studies (Table S1). The retention times are coincident with enhanced light absorption in the eluates of chamber filters and the same trend of higher-order oligomers eluting later in the chromatographic run is observed. In the chamber experiments, the 3-MeTHF-3,4-diols formed exclusively under acidic conditions and correlated with filter browning. The 3-MeTHF-3,4-diols at field sites (up to 57.7 ng m^{-3}) are present in samples where high DBE oligomers

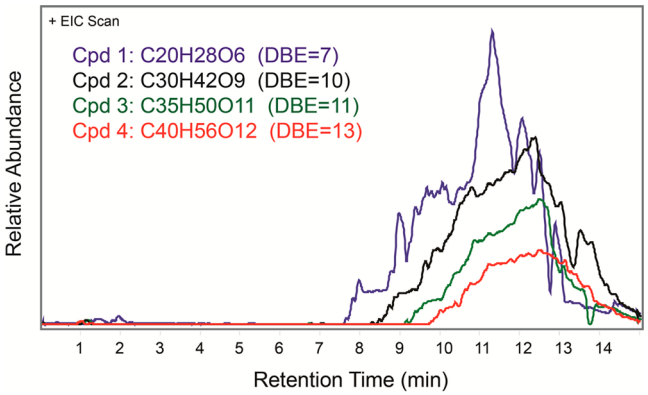

Figure 5. Observations of IEPOX-derived light-absorbing oligomers in ambient fine aerosols collected from the southeastern U.S. region (Yorkville, GA) during the summer of 2010.

are detected,[9] and low aerosol pH has been reported for atmospheric particulates under the influence of anthropogenic SO_2 emissions. Consistency between field and chamber analyses thus support the atmospheric relevance of our chamber findings. Additionally, the more hydrated forms of oligomeric species observed in the chamber studies are also observed in the field samples collected from the same region.

Atmospheric Implications. Light-absorbing oligomeric SOA constituents characterized in this study from both laboratory and field samples reveal the potential significance of IEPOX as a previously unidentified source for regional BrC formation over the rural Southeastern U.S. in summer when the influence of biomass burning is low.[11,12] Formation of IEPOX-derived BrC observed under dry and acidic conditions in our chamber experiments implies that the ongoing heterogeneous and aerosol-phase chemistry leading to BrC formation facilitated by aerosol acidity is a kinetic-limited process. Further investigation of IEPOX-derived BrC formation via extended chemical aging is needed to elucidate the kinetic effects and the formation processes under atmospherically relevant scenarios. Identification of oligomeric species at the molecular level in ambient aerosols linked to IEPOX pathways adds to the current understanding of unresolved organic aerosol mass in regions impacted by high isoprene emissions under low-NO_x conditions. Quantification of known isoprene SOA tracers can explain ~60−70% organic aerosol mass from current chamber experiments. A recent comparison of field measurements with a modeling simulation based on currently known IEPOX chemistry predicts much less mass than observed in the field.[54] The observations of oligomers in SOA also have important implications for the aerosol phase state that affects the rate of heterogeneous reactions and mass accommodation. Together with recent aircraft data showing BrC can contribute to ~20% of the radiative forcing in this region,[13] understanding of the proportion of measured BrC in this region attributable to the IEPOX pathway is important for improving current climate model representation, and assessing the impact of BrC on regional climate.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional discussion regarding quality assurance for off-line chemical analyses, tentatively proposed mechanisms, and descriptions for $PM_{2.5}$ sampling during the 2013 Southern Oxidant and Aerosol Study (SOAS) is provided. Detailed

accurate mass fittings for measured ions from chamber experiments and field samples are listed in Tables S1−S2. UV−vis spectra from UPLC/DAD and bulk measurements are provided in Figure S1. Comparisons of the light absorbance and characterized SOA tracers are provided in Figure S2. Additional mass spectra and proposed structures are shown in Figures S3−S5. Figure S6 provides extracted ion chromatograms of identified oligomer series from chamber samples. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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