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Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of Long-Chain Alkanes

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Abstract

We report the formation of aliphatic organosulfates (OSs) in secondary organic aerosol (SOA) from the photooxidation of C_{10} – C_{12} alkanes. The results complement those from our laboratories reporting the formation of OSs and sulfonates from gas-phase oxidation of polycyclic aromatic hydrocarbons (PAHs). Both studies strongly support formation of OSs from gas-phase oxidation of anthropogenic precursors, hypothesized on the basis of recent field studies in which aromatic and aliphatic OSs were detected in fine aerosol collected from several major urban locations. In this study, dodecane, cyclodecane and decalin, considered to be important SOA precursors in urban areas, were photochemically oxidized in an outdoor smog chamber in the presence of either non-acidified or acidified ammonium sulfate seed aerosol. Effects of chemical structure, acidity and relative humidity on OS formation were examined. Aerosols collected from all experiments were characterized by ultra performance liquid chromatography coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS). Most of the OSs identified could be explained by formation of gaseous epoxide precursors with subsequent acid-catalyzed reactive uptake onto sulfate aerosol. The OSs identified here were also observed and quantified in fine urban aerosol samples collected in Lahore, Pakistan, and Pasadena, USA. Many of the OSs identified from the photooxidation of decalin and cyclodecane are isobars of known monoterpene organosulfates, and thus care must be taken in the analysis of alkane-derived organosulfates in urban aerosol.

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1. Introduction

Atmospheric fine particulate matter ($PM_{2.5}$, aerosol with aerodynamic diameter ≤ 2.5 μm) plays a major role in scattering and absorption of solar radiation, which impacts global climate (Kroll and Seinfeld, 2008; Stevens and Boucher, 2012). $PM_{2.5}$ also participates in heterogeneous chemical reactions, affecting the abundance and distribution of atmospheric trace gases (Hallquist et al., 2009). Human exposure to $PM_{2.5}$ is associated with respiratory and cardiovascular diseases (Elder and Oberdorster, 2006).

Typically, the largest mass fraction of $PM_{2.5}$ is organic, dominated by secondary organic aerosol (SOA) formed by the oxidation of volatile organic compounds (VOCs). Although SOA contributes a large fraction (20–90%, depending on location) of total $PM_{2.5}$ mass, current models predict less SOA than is generally observed during field measurements (Kroll and Seinfeld, 2008; Hallquist et al., 2009). The underestimate is largely a consequence of omission of intermediate volatility organic compounds (IVOC), such as alkanes or polycyclic aromatic hydrocarbons (PAHs) (Pye and Pouliot, 2012; Tkacik et al., 2012) as SOA precursors. Long-chain alkanes are important anthropogenic pollutants emitted by combustion and vehicular sources representing up to 90% of the anthropogenic emissions in certain urban areas (Fraser et al., 1997, Gentner et al., 2012). In the atmosphere, they are rapidly depleted by reaction with OH and NO_3 radicals (Atkinson, 2000) yielding a large variety of oxygenated compounds (Lim and Ziemann, 2005; 2009; Yee et al., 2012), which could lead to SOA formation (Lim and Ziemman, 2009; Loza et al., 2014). SOA yields have been measured for C_7-C_{25} alkanes having linear, branched and cyclic structures (Lim and Ziemman, 2009; Presto et al., 2010; Loza et al., 2014; Hunter et al., 2014). Structure plays a key role in SOA yield, which increases with carbon number or the presence of cyclic features and tends to decrease with branching as gas-phase fragmentation predominates (Carrasquillo et al., 2014; Loza et al., 2014; Hunter et al., 2014).

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The presence of organosulfates (OSs) has been demonstrated in several atmospheric compartments, including atmospheric aerosol (Iinuma et al., 2007; Gómez-González et al., 2008; Hawkins et al., 2010; Hatch et al., 2011; Kristensen et al., 2011; Stone et al., 2012; Shalamzari et al., 2013; Hansen et al., 2014; Liao et al., 2015), rain (Altieri et al., 2009), clouds and fog (Pratt et al., 2013; Boone et al., 2015) and several studies indicate that OSs could contribute a substantial fraction (up to 30%) of the organic mass measured in ambient $PM_{2.5}$ (Surratt et al., 2008; Tolocka and Turpin, 2012).

Although the variety of OSs identified from field measurements is quite large (Surratt et al., 2008; Tao et al., 2014; Kuang et al., 2015; Wang et al., 2015), only a few OS precursors have been unequivocally identified through laboratory studies. OSs have been generated in SOA in smog chambers from OH, NO_3 or O_3 oxidation of BVOCs, including isoprene (Surratt et al., 2007, Ng et al., 2008), 2-methyl-3-buten-2-ol (MBO) (Zhang et al., 2012; Mael et al., 2015), unsaturated aldehydes (Schindelka et al., 2013; Shalamzari et al., 2014; Shalamzari et al., 2015), monoterpenes (Iinuma et al., 2007; Iinuma et al., 2009; Surratt et al., 2008), and sesquiterpenes (Liggio et al., 2006; Surratt et al., 2008; Iinuma et al., 2009; Noziere et al., 2010; Chan et al., 2011) in the presence of acidified sulfate aerosol. However, the large number of unidentified OSs having C_2 to C_{25} skeletons observed in recent field studies are clearly not derived from BVOC precursors, and suggest alkanes and aromatics as a major source of hitherto unrecognized of OS precursors (Tao et al., 2014; Kuang et al., 2015; Wang et al., 2015). Ma et al. (2014) have recently shown that the contribution of aromatic OSs could represent up to two-thirds of the OSs identified in Shanghai. Aliphatic OSs were identified in the ambient samples from urban locations (Tao et al., 2014; Kuang et al., 2015; Wang et al., 2015), suggesting that gas-phase oxidation of long-chain or cyclic alkanes could be an important source of OSs (Tao et al., 2014). At present, lack of authentic standards currently

prevents quantitation of the OSs contribution to $PM_{2.5}$ mass, underscoring the need to better identify the OS precursors.

Studies on the impact of NO_x and O_3 on SOA formation from oxidation of long-chain alkanes (Loza et al., 2014; Zhang et al., 2014) have shown that the presence of NO_x tends to reduce SOA formation by reaction of peroxy radicals (RO_2) with NO, to yield alkoxy radicals (RO). For alkanes containing fewer than 10 carbons, the fragmentation/decomposition of RO radicals will produce higher volatility species (e.g., small carbonyls), which suppresses or reduce SOA formation (Lim and Ziemann, 2005, 2009). Recent studies have shown that increased aerosol acidity is a key variable in enhancing SOA formation through acid-catalyzed reactive uptake and multiphase chemistry of oxidation products derived from biogenic VOCs (BVOCs) such as isoprene (Surratt et al., 2010) and α-pinene (Iinuma et al., 2009); however, no such studies have been reported for the oxidation of alkanes. Formation of highly oxidized products, including OSs, demonstrates the importance of heterogeneous processes, such as reactive uptake of epoxides onto acidic sulfate aerosol, in SOA formation (Iinuma et al., 2009; Surratt et al., 2010; Chan et al., 2011; Lin et al., 2014; Shalamzari et al., 2015). OSs may also be formed by either nucleophilic substitution of organic nitrates by sulfate (Darer et al., 2011; Hu et al., 2011) or by heterogeneous oxidation of unsaturated compounds involving sulfate anion radicals (Noziere et al., 2010; Schindelka et al., 2013; Schone et al., 2014).

Formation of OSs from the gas-phase oxidation of the C_{10} alkanes, cyclodecane ($C_{10}H_{20}$) and decalin (bicyclo[4.4.0]decane; $C_{10}H_{18}$), and C_{12} alkane, dodecane ($C_{12}H_{26}$), in the presence of sulfate aerosol under varying acidities is reported in this work. Effects of RH, aerosol acidity and alkane structures on OS formation were investigated. SOA collected from outdoor smog chamber experiments was chemically characterized by ultra performance liquid chromatography interfaced to high-resolution quadrupole time-of-flight mass spectrometry

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equipped with electrospray ionization (UPLC/ESI-HR-QTOFMS). In addition, effect of solvent mixture (methanol vs acetonitrile/toluene) on OS quantification was investigated. Finally, $PM_{2.5}$ samples collected from Lahore, Pakistan and Pasadena, USA were analyzed to detect and quantify OSs identified from the smog chamber experiments.

2. Experimental

2.1 Chamber Experiments. Eighteen experiments were performed at the University of North Carolina (UNC) outdoor smog chamber facility located at Pittsboro, NC. Details of this facility have been previously described (Lee et al., 2004; Kamens et al., 2011). Briefly, it is a 274−m^3 dual chamber divided into two sides by a Teflon film curtain. One side referred as "North Chamber" has an actual volume of 136 m^3, and the other side referred as "South Chamber" has an actual volume of 138 m^3. Prior to each experiment, both sides of the chamber were flushed using rural background air using an exhaust blower for at least 12 hours. Clean air was then injected into both sides of the chamber using a clean air generator to reduce concentrations of background aerosol and VOCs. Experiments were performed under two humidity conditions: at low RH (10−20%) and high RH (4−60%). For experiments conducted at low RH (i.e., dry), the clean air generator was used after the preliminary venting using rural air for approximately 48−72 hours. A scanning mobility particle sizer (SMPS, TSI 3080) was used to measure aerosol size distributions, including number and volume concentrations inside both chambers. Before each experiment, the typical aerosol mass concentration (assuming an aerosol density of 1 g cm^{-3}) background was less than ~ 3 μg m^{-3} in humid conditions and less than ~ 0.2 μg m^{-3} for dry experiments. Either non-acidified or acidified ammonium sulfate seed aerosols were introduced into the chambers by atomizing aqueous solutions of 0.06 M $(NH_4)_2SO_4$ or 0.06 M $(NH_4)_2SO_4$ + 0.06 M H_2SO_4, respectively. After 15 min of atomization, ~ 40 μg m^{-3} of seed aerosol was injected into the chambers.

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After stabilization of aerosol volume concentrations, Teflon filters were collected (47 mm diameter, 1.0 μm pore size, Tisch Environmental, EPA $PM_{2.5}$ membrane) over 45 min at a sampling rate of ~ 25 L min^{-1} in order to measure baseline aerosol composition prior to injection of the SOA precursors. None of the aliphatic OSs produced from the oxidation of studied alkanes were detected in the chamber background. Dodecane (Sigma-Aldrich, 99%), cyclodecane (TCI, 94%) or decalin (Sigma-Aldrich, 99%, mixture of *cis* + *trans*) were introduced into both sides of the chamber by passing a N_2 flow through a heated manifold containing a known amount of liquid compound. Concentrations of alkanes were measured online in each side every 10 minutes by a gas chromatograph with a flame ionization detector (GC−FID, Model CP-3800, Varian), calibrated before each experiment with a standard mixture of hydrocarbons. Isopropyl nitrite (IPN) (Pfaltz & Bauer, 97%) was used as an OH radical precursor (Raff and Finlayson-Pitts, 2010) and was injected into both sides when VOC signals were stable as measured by the GC−FID. O_3 and NO_x concentrations were monitored using UV photometric and chemiluminescent analyzers, respectively (O_3: Model 49P, Thermo-Environmental; NO_x: Model 8101B, Bendix). Both instruments were calibrated as described in previous work (Kamens et al., 2011). Dilution rate for each chamber was monitored by sulfur hexafluoride (SF_6) measured using gas chromatography with electron capture detection (GC−ECD). RH, temperature, irradiance and concentration of O_3 and NO_x were recorded every minute. SOA formation from alkane photooxidation was monitored for all experiments. 2−3 hours following IPN injection, which corresponds to the end of SOA growth as measured by the SMPS, filter sampling was initiated. For each experiment, two filters from each side of the chamber were collected for 45 min − 2 hours (sampling rate ~ 25 L min^{-1}) to characterize particle-phase reaction products. Based on SOA volume concentrations measured by the SMPS, sampling time was adjusted to obtain an SOA mass of about ~ 100 μg/filter. Experimental conditions are summarized in Table 1.

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2.2 Ambient Aerosol Collection. Five filters collected in Lahore (Pakistan) between January 2007 and January 2008 (Stone et al., 2010) and eight filters collected in Pasadena (USA) during the 2010 California Research at the Nexus of Air Quality and Climate Change (CalNex) field study from 15 May − 15 June 2010 (Hayes et al., 2013), were analyzed for the OSs identified in smog chamber experiments. $PM_{2.5}$ was collected on prebaked quartz fiber filters (QFF, Pall Life Sciences, Tissuquartz, 47 mm for Lahore, 20.3 cm × 25.4 cm for Pasadena) using a medium-volume sampling apparatus at Lahore (URG-3000, Chapel Hill, NC, USA) and a high-volume sampler (Tisch Environmental, Cleves, OH, USA) at Pasadena. As stipulated previously at both urban sites, anthropogenic activities (e.g., vehicular exhaust, industrial sources, cooking, etc.) likely dominated the organic aerosol mass fraction of $PM_{2.5}$ (Stone et al., 2010; Hayes et al., 2013).

2.3 Filter Extraction. The impact of the solvent mixture on OS quantification was also explored in this work. Filters collected from smog chamber experiments were extracted using two different solvent mixtures. One filter was extracted using 22 mL of high-purity methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich, ≥ 99.9 %) under 45 min (25 min + 20 min) of sonication at room temperature while the second filter was extracted using 22 mL of a 70/30 (v/v) solvent mixture containing acetonitrile/toluene (CHROMASOLV-grade, for HPLC, Sigma-Aldrich, ≥ 99.9 %). Extracts were then blown dry under a gentle nitrogen stream at ambient temperature (Surratt et al., 2008; Zhang et al., 2011; Lin et al., 2012). Dry extracts were then reconstituted with 150 μL of either a 50:50 (v/v) solvent mixture of methanol and water (MilliQ water) or a 50:50 (v/v) solvent mixture of acetonitrile and water. Filters collected from field studies were extracted using methanol as solvent mixture and following the protocol described above; however, prior to drying, extracts were filtered through 0.2-μm PTFE syringe filters (Pall Life Science, Acrodisc) to remove insoluble particles or quartz filter fibers.

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2.4 Chemical Analysis. Characterization of OSs in chamber experiments was performed using ultra performance liquid chromatography interfaced to a high-resolution quadrupole time-of-light mass spectrometer equipped with an electrospray ionization source (UPLC/ESI-HR-Q-TOFMS, 6500 Series, Agilent) operated in the negative ion mode. Exact operating conditions have been previously described (Lin et al., 2012). 5 μL sample aliquots were injected onto a UPLC column (Waters ACQUITY UPLC HSS T3 column). Octyl sulfate ($C_8H_{17}O_4S^-$; Sigma-Aldrich) and 3-pinanol-2-hydrogen sulfate ($C_9H_{13}O_6S^-$) were used as surrogate standards to quantify the identified aliphatic OSs.

3. Results and Discussion

In the subsequent sections, detailed chemical characterization of OSs identified from the gas-phase oxidation of dodecane, decalin and cyclodecane in the presence of ammonium sulfate aerosol is presented. The presence of OSs was revealed by the appearance of characteristic fragment ions at *m/z* 79.95 ($SO_3^{\bullet/-}$), 80.96 (HSO_3^-) and/or 96.96 (HSO_4^-) in tandem mass spectra (MS^2) (Iinuma et al., 2007; Gómez-González et al., 2008; Surratt et al., 2008; Shalamzari et al., 2013; 2014). Tentative structures, retention times and exact mass measurements of OSs detected in this work are reported in Table S1. The low abundance of some OSs precluded acquisition of high-resolution MS^2 data, and thus, structures have not been proposed for these less-abundant parent ions.

3.1 Characterization of OSs from Dodecane Photooxidation. Seven OSs, including isobaric compounds, were identified in SOA produced from the gas-phase oxidation of dodecane in the presence of sulfate seed aerosol. None have previously been reported in chamber experiments, although they have recently been observed in ambient fine aerosol samples (Tao et al., 2014; Kuang et al., 2015). Concentrations of the products are reported in Table S2. Three isobaric parent ions with *m/z* 279 ($C_{12}H_{23}O_5S^-$, 279.1254) were identified in SOA generated from dodecane oxidation in the presence of acidified ammonium sulfate

aerosol. Based on Yee et al. (2012; 2013) the products are tentatively assigned as 1,3-dodecanone sulfate isomers. The MS^2 spectra of the products were identical, having product ions diagnostic for a sulfate ester β to an abstractable proton (Surratt et al., 2008; Gómez-González et al., 2008) at *m/z* 199 ($C_{12}H_{23}O_2^-$, loss of neutral SO_3) and 97 (HSO_4^-), precluding assignment of positional isomerism. A study on the OH oxidation of the linear alkane octacosane indicates a strong preference for oxidation at terminal carbons, with the C_2 carbonyl predominating (Ruehl et al., 2013), suggesting the structure 2-dodecanone-4-sulfate for OS-279 and possibly 3-dodecanone-5-sulfate and 4-dodecanone-6-sulfate isomers as isobaric ions. Figures 1 and S1 present the MS^2 spectrum of OS-279 and proposed fragmentation pathway, respectively. By chemical ionization mass spectrometry (CIMS) operating in the negative mode, Yee et al. (2012) identified the formation of hydroperoxides from the oxidation of dodecane under low–NO_x conditions, confirming the predicted RO_2 – HO_2 reaction pathway in the low–NO_x regime. First-generation hydroperoxides can react with OH by further oxidation to form low–volatility, more highly oxidized products or by fragmentation/decomposition of alkoxy (RO) radicals to form products with higher volatility (Yee et al., 2012, Carrasquillo et al., 2014). In our study, OH radicals were formed from IPN photolysis without additional injection of NO. Under these conditions, RO_2 chemistry is dominated by RO_2 + HO_2 and/or RO_2 + RO_2 reactions as discussed by Raff and Finlayson-Pitts (2010). Although RO_2 radicals formed in the first oxidation step could also react with NO formed by IPN photolysis, significant formation of ozone under chamber conditions (0.3-0.6 ppm, depending on concentration of IPN injected) would rapidly quench NO. Thus RO_2 + NO reactions are not anticipated to be significant (Raff and Finlayson-Pitts, 2010). Carbonyl hydroperoxide (CARBROOH), which has been identified in the gas phase by Yee et al. (2012), is likely involved in acid-catalyzed reactive uptake onto sulfate aerosol. Heterogeneous chemistry of gas-phase organic peroxides has been previously suggested to

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explain the formation of certain OSs and tetrols (Claeys et al., 2004; Riva et al., 2015b). Acid-catalyzed perhydrolysis of hydroperoxides followed by reaction with sulfate anion radicals could also be possible route to the formation of OS-279 (Figure 1). However, further investigation is required to better understand how acidified sulfate seed aerosol takes up organic peroxides from the gas phase and how particle-phase reactions might degrade organic peroxides into OSs.

3.2 Characterization of OSs from Decalin Photooxidation. Gas-phase oxidation of cyclic alkanes at room temperature and atmospheric pressure has received less attention than linear or branched alkanes. However, recent studies have demonstrated that oxidations of cyclic alkanes by OH radicals produce less–volatile oxygenated compounds and have larger SOA yields (Yee et al., 2013; Hunter et al., 2014). Significant formation of OSs (up to 1 μg m^{-3}) and SOA were observed in all experiments of decalin photooxidation (Tables 1 and S3), revealing the high potential for bicyclic alkanes to form OSs. All OSs (25 OSs including isomeric/isobaric structures) identified from the oxidation of decalin in the presence of ammonium sulfate aerosol have been observed in ambient aerosol, underscoring the potential importance of alkanes to OS formation in urban areas (Tao et al., 2014; Kuang et al., 2015; Wang et al., 2015). MS^2 spectra were obtained for all OSs identified from decalin oxidation, except for parent ions at *m/z* 195.0697 (OS-195) and 299.0805 (OS-299). All of the parent ions show an intense product ion at *m/z* 96.96, indicative of an aliphatic sulfate ester. Retention times and tentative structural assignments are given in Table S1.

Figures 2 and S2 present MS^2 spectra and fragmentation schemes of selected parent ions at *m/z* 265.0749 (OS-265), 269.0696 (OS-269), 295.0494 (OS-295) and 326.0554 (OS-326). MS^2 spectra and fragmentation schemes of other OSs are reported in Figure S3-S7. These selected OSs exhibit specific fragmentation patterns and were, as described in the next section, quantified and characterized in the fine urban aerosol samples. Four isomers of OS-

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265 with composition $C_{10}H_{17}O_6S^-$ were identified in decalin-derived SOA collected from all experiments. With regard to components of ambient SOA, it is important to mention that the formation of isobaric OSs with the same elemental composition of $C_{10}H_{17}O_6S^-$ isobars have also been previously identified in SOA produced from the gas-phase oxidation of monoterpenes (Liggio et al., 2006; Surratt et al., 2008) and are not unique to decalin oxidation. The product ion at nominal *m/z* 97 (HSO_4^-) and loss of neutral SO_3 in the MS^2 spectrum (Figure 2a) is consistent with an aliphatic OS having a labile proton in a β position (Attygalle et al., 2001). Absence of product ions corresponding to a loss of a terminal carbonyl (−CO) or a carboxyl group (−CO_2), respectively (Romero and Oehme, 2005; Shalamzari et al., 2014), and a composition corresponding to 2 double bond equivalencies (DBEs) has thus been attributed to an internal carbonyl group and a six-membered ring. A scheme leading to the structure proposed in Figure 2a is based on the abstraction of H at the ring fusion and C_1–C_2 bond cleavage (Figure S8, pathway **a**) and subsequent reaction with O_2 followed by 1,5-H shifts leading to an epoxide and sulfate ester by reactive uptake/heterogeneous chemistry.

The composition of the parent ion at *m/z* 269.0696 ($C_9H_{17}O_7S^-$) corresponds to one DBE. MS^2 spectrum yields products consistent with a sulfate ester β to an abstractable proton and similar to OS-265, neither a terminal carbonyl nor a carboxyl functional group was detected in the OS-269. As a result, the presence of hydroperoxide and/or hydroxyl substituents is expected in order to help explain this molecular formula obtained from the accurate mass measurement. In Figure 3, tentative pathways leading to the formation of OS-267, OS-269 and OS-285 are proposed. Under low-NO_x conditions abstraction of a proton α to the ring fusion of decalin followed by reaction with O_2 leads to the 1-hydroperoxy radical (Yee et al., 2013; Schilling Fahnestock et al., 2015), which in turn can react with another RO_2 radical to yield the corresponding alkoxyl radical ($C_{10}H_{17}O^{\bullet}$) (Atkinson, 2000). Cleavage of

the C_1–C_2 decalin bond, followed by reaction with a second O_2 molecule and HO_2 leads to a terminal carbonyl hydroperoxide (tCARBROOH; $C_{10}H_{18}O_3$). As reported in recent studies, the resulting RO_2 radical can undergo isomerization/auto-oxidation to yield a hydroperoxide (Ehn et al., 2014; Jokinen et al., 2014; Mentel et al., 2015), which can lead to the formation of OSs through reactive uptake (Mutzel et al., 2015). By analogy to other aldehydes, OH preferentially abstracts the tCARBROOH aldehydic H (79:21 branching ratio; Kwok and Atkinson 1995). The RO_2 radical produced from H–atom could react with RO_2 or HO_2 and form an acyl-oxy radical ($R(O)O^{\bullet}$), which decarboxylates quickly (Chacon-Madrid et al., 2013) to a hydroperoxyperoxy radical ($C_9H_{17}O_4^{\bullet}$). The hydroperoxyperoxy radical can react via pathway **a** (Figure 3) leading to OS-267, previously unreported, or OS-269 or pathway **b** (Figure 3) leading to OS-285. Pathway **a** proceeds via a 1,7-H shift followed by elimination of OH from the resulting dihydroperoxy alkyl radical to give a dihydroperoxyepoxide by a 1,5-H shift and OH elimination analogous to the formation of isoprene epoxydiol (IEPOX) (Paulot et al., 2009; Mael et al., 2015). The epoxide can then undergo acid-catalyzed ring opening to give OS-269, which may be further oxidized to OS-267. The MS^2 spectrum of OS-285 (Figure S5) shows product ions corresponding to HSO_3^-, HSO_4^- and loss of neutral SO_3, in accord with a sulfate ester β to a labile proton, but yields no further structural information. The structure proposed for OS-285 is based on the reaction of the hydroperoxyperoxyl radical intermediate in pathway **a** with RO_2 followed by a 1,6-H shift and addition of O_2 to give a hydroxyhydroperoxyperoxyl radical ($C_9H_{17}O_5^{\bullet}$) leading to an epoxide by a 1,5-H shift and OH elimination as described above (Iinuma et al., 2009; Surratt et al., 2010; Jacobs et al., 2013; Mael et al., 2015).

In Figure 4, pathways from an initial 1-peroxy transient are proposed to products designated OS-295, OS-311 and OS-326. Three isobaric ions corresponding to OS-295 ($C_{10}H_{15}O_8S^-$) were identified in decalin-derived SOA under all experimental conditions.

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Figure 2c shows the MS^2 spectrum of the parent ion at *m/z* 295. A product ion at *m/z* 251 corresponding to loss of CO_2 (Romero and Oehme, 2005; Shalamzari et al., 2014) is present in addition to product ions consistent with a sulfate ester β to a labile H (Riva et al., 2015b). Pathway **a** leads to the structure consistent with the MS^2 spectrum and 3 DBEs required by the composition of the parent ion. The salient features of pathway **a** include oxidation of the RO_2 to 2-decalinone, formation of a C_{10} alkoxy radical followed by ring cleavage of the C_9–C_{10} decalin bond leading to a 4-(carboxy cyclohexyl)-1-hydroperoxybut-2-yl radical via RO_2 chemistry, and a 1,7-H shift and acid-catalyzed ring opening of the epoxide resulting from the addition/isomerization of the O_2 adduct (Paulot et al., 2009).

Two isobaric parent ions with identical MS^2 spectra were observed at *m/z* 311 (Figure S7). The only observed product ion at *m/z* 97 is consistent with a sulfate ester, but not informative with regard to a more refined assignment of molecular structure. Pathway **b** to a hydroperoxide for the parent ion with 3 DBEs is proposed by analogy to the putative hydroperoxide structures of OS-267, OS-269 and OS-285. Pathway **b** is characterized by a H-abstraction from a carbon at the ring fusion of 2-decalinone leading to formation of an 2-decalinone-6-oxyl radical followed by a sequence of ring cleavage, O_2 additions and H-shifts to form a 4-(2,6-cyclohexyl)-2-hydroperoxybutan-1-oxide that can form the sulfate ester on reactive uptake. Abstraction of H_1 rather than H_6 would lead to an isobaric structure.

Four isobaric ions corresponding to $C_{10}H_{16}NO_9S^-$ with identical MS^2 spectra (Figure 1d) were detected at nominal mass *m/z* 326. The loss of 63 mass units as neutral HNO_3 (Figure S2d) is in accord with a nitrate ester (Surratt et al., 2008), supported by the absence of product ions from loss of NO or NO_2 (Kitanovski et al., 2012). Pathway **c**, to the parent ion at *m/z* 326 proceeds from the reaction of the decalin-2-peroxy radical with NO to form decalin-2-nitrate ($C_{10}H_{17}NO_3$) (Atkinson, 2000). From this point, a sequence of reactions identical to pathway **b** yields the parent OS-326. It is important to mention that the formation of isobaric

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OSs with the same elemental composition of $C_{10}H_{16}NO_9S^-$ isobars have also been identified in SOA produced from the gas-phase oxidation of monoterpenes (Surratt et al., 2008).

The MS^2 spectrum for the single parent ion at *m/z* 281 corresponding to the composition $C_{10}H_{17}O_7^-$ (OS-281) gave product ions expected for a sulfate ester β to a labile proton with 2 DBE, but no additional structural information (Figure S4). The pathway proposed in Figure S8 pathway **b** is based on gas-phase oxidation of to a 4-(cyclohexan-2-one)but-1-yl radical followed by reaction with O_2 and a 1,6-H shift followed by addition of a second O_2, a 1,5-H shift and elimination of OH to give an epoxide. The direction of ring opening of the internal epoxide by reactive uptake to give the final product is arbitrary. Three isobaric parent ions at *m/z* 297 corresponding to the composition $C_{10}H_{17}O_8S^-$ with 2 DBEs were identified. Loss of water, HSO_4^- and SO_3 as a neutral fragment in the MS^2 spectrum of the major isobar (OS-297) is consistent with a hydroxyl-substituted sulfate ester β to a labile proton (Figure S6). The scheme proposed in Figure S8 pathway **c** is based on the oxidation to a 4-(cyclohexan-2-one)but-1-yl radical as in pathway **b**. However, in contrast to pathway **b**, RO_2 formed by the addition of O_2 undergoes a 1,6-H shift followed by addition of a second O_2 molecule, a 1,5-H shift and elimination of OH to yield an epoxide, which be reactively taken up to give a sulfate ester. The direction of ring opening of the internal alkyl epoxide is arbitrary.

3.3 Characterization of OSs from Cyclodecane Photooxidation. The concentrations of OSs identified from gas-phase oxidation of cyclodecane are reported in Table S4. High levels of OSs were observed in experiments performed under dry conditions with acidified ammonium sulfate seed aerosol. The impact of acidity on OS formation will be discussed in more detail in the following section. The MS^2 spectra of all cyclodecane products show only a single product ion at nominal *m/z* 97 corresponding to bisulfate (Figures S9 – S13), indicating that the oxidation products are sulfate esters β to a labile proton. None of the fragment ions

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observed in the MS^2 spectrum suggests neither a terminal carbonyl nor a carboxyl functional group are present in the cyclodecane-OSs, consistent with retention of the cyclodecane ring the oxidation products. Tentative structures proposed in Table S1 are based on DBE calculations and retention of the cyclodecane ring supported by MS^2 data. Pathways proposed in Figures S14 and S15 are initiated by H-abstraction and based on reaction sequences for which precedent has been established: addition of O_2 to cycloalkyl radicals to give RO_2 which either react with RO_2 to yield alkoxy radicals (Atkinson, 2000; Yee et al., 2012) or undergo intramolecular H-shifts leading to generation of hydroperoxydes (Ehn et al., 2014; Jokinen et al., 2014). The formation of compounds such as cyclodecanone ($C_{10}H_{18}O$) or cyclodecane hydroperoxide ($C_{10}H_{20}O_2$) are proposed as intermediate products leading to epoxy-compounds after additional oxidation/isomerization processes, as presented in Figures S14 and S15. Since authentic standards are unavailable and the MS^2 data do not allow specific structural features to be assigned, the end products in pathways in Figures S14 and S15 are arbitrary. Isobars may be explained by *cis*/*trans* epoxide ring opening or the span of an H-shift (1,5-,1,6- and 1,7-H shifts are possible). In the case of OS-249, where *cis*/*trans* isomers are not possible; the two isobaric structures may result from different H-shifts. OS-265 and OS-281 are reported here for the first time in chamber studies.

3.4 Effect of Alkane Structure on Relative SOA Yield. Alkane structures appear to be important determinants of the relative yields of OSs from dodecane, decalin and cyclodecane photooxidation. Tables S2-S4 show that OS concentrations are significantly higher from the photooxidation of decalin and cyclodecane than from dodecane. As reported in Table 1, SOA formation from gas-phase oxidation of decalin and cyclodecane was much higher than during photooxidation of dodecane, which could explain the larger amount of OSs identified. Although the SOA formed from photooxidation of both cyclic alkanes was comparable, the

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sum of OSs quantified from oxidation of decalin was 3-4 times higher. An investigation of the reason for these differences is ongoing.

3.5 Impact of Relative Humidity and Acidity on OS Formation. Experiments were performed under conditions reported in Table 1. As shown in Figure 5 and Tables S2-S4, the presence of acidic aerosols significantly increases OS formation in most cases, as previously observed for OSs in SOA generated from biogenic sources (Iinuma et al., 2007; Surratt et al., 2007; Chan et al., 2011). Since differences in meteorology could impact experimental results from the outdoor chamber, caution must be exercised in comparing experiments performed on different days. However, same-day, side-by-side experiments allow for clear resolution of the effects of aerosol acidity and seed composition on OS formation. When comparing experiments performed under dry versus wet conditions with acidified ammonium sulfate aerosol, higher RH conditions significantly reduce OS formation, likely attributable to an increase in pH because of dilution by additional particle water. To better investigate the effect of acidity on OS formation, products were divided in two groups (Figure 5), those whose concentrations were increased by a factor ≥ 2 (Group-1) and ≤ 2 (Group-2). Figure 5 and Tables S2-S4 show that OSs identified from dodecane photooxidation belong to Group-2, with the exception of OS-279. OSs from decalin photooxidation, including OS-195, OS-269 and OS-297 belong to Group-2 as well. OSs can be formed via different pathways, including acid-catalyzed ring-opening reactions of epoxy-containing SOA constituents, reactive uptake of unsaturated compounds into the particle phase, or by reaction with the sulfate anion radical (Rudzinski et al., 2009; Nozière et al., 2010; Schindelka et al., 2013; Schöne et al., 2014). OSs may also result from nucleophilic substitution of nitrate by sulfate (Darer et al., 2011; Hu et al., 2011). The impact of acidity on OS formation arising from the different pathways has been investigated principally for reactive uptake of epoxy-compounds (Jacobs et al., 2013; Lin et al., 2012; Gaston et al., 2014; Riedel et al., 2015) for which OS formation is strongly

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enhanced under acidic conditions (Lin et al. (2012). However, a similar enhancement was not observed in our study on PAH-OSs, which were not expected to result from epoxide chemistry (Riva et al., 2015a). Based on these observations, the formation of Group-1 OSs are hypothesized to be products of reactive uptake of gas-phase epoxides.

3.6 Impact of Solvent Mixture on OS Quantification. Additional filters were collected from each side of the outdoor chamber and for each experiment to investigate the impact of solvent mixture on OS quantification. Tao et al. (2014) have recently reported that less polar solvents such as an acetonitrile (ACN)/toluene mixture are a better choice for extraction of long alkyl-chain OSs from filters using a nanospray-desorption electrospray ionization mass spectrometry where the extraction occurs *in situ* and the analyses are qualitative. Figure 6 demonstrates that, overall, concentrations of OSs (ng m^{-3}) from the photooxidation of dodecane, decalin and cyclodecane seem to be more efficiently extracted by the ACN/toluene mixture. Tables S2-S4, showing the ratios of the concentrations individual OSs extracted by the ACN/toluene mixture divided by the concentration of OSs extracted by methanol, indicates that all C_{10}− and C_{12}− OS products, including highly oxidized OS, appear more efficiently extracted by the ACN/toluene mixture. For OSs smaller than C_{10}, extraction efficiencies are about the same. As noted above, isobars of OSs identified from the oxidation of alkanes have been observed in SOA generated from the oxidation of monoterpenes that are currently used as tracers for monoterpene SOA chemistry (Hansen et al., 2014; Ma et al., 2014). Hence, in addition to the caution that quantitation of alkane and monoterpene OSs is uncertain in the absence of authentic standards, some monoterpene OSs may be underestimated if not fully extracted because most studies use methanol as an extraction solvent (Surratt et al., 2008; Iinuma et al., 2009). More work is, however, needed to better characterize and elucidate the impact of solvent on the quantitation of biogenic and anthropogenic OSs, especially compounds > C_{10}.

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3.7 OSs Derived from Long-Chain Alkanes in Ambient Fine Urban Aerosol. Archived fine urban aerosol samples collected at Lahore, Pakistan, and Pasadena, USA were used to evaluate and quantify OSs identified in SOA produced from the photooxidation of long-chain alkanes. Filters were initially extracted using methanol and comparison to OSs quantified using another solvent mixture was not possible. As previously mentioned, seven parent ions have been observed in laboratory studies. Therefore, extracted ion chromatograms (EICs) obtained from smog chamber experiments were compared to those obtained from both urban locations to confirm that observed OSs correspond to OSs identified in our lab study. Figures 7 and S16 present the EICs of OSs observed in both ambient and our smog chamber-generated SOA. Table 2 identifies 12 OSs, along with concentrations, present in $PM_{2.5}$ collected from Lahore, Pakistan and Pasadena, USA and also observed in our smog-chamber-generated SOA.

The high concentrations, especially at Lahore (Pakistan) of the OSs measured in the ambient aerosol samples support their use as tracers for SOA produced from the oxidation long-chain alkanes in urban areas. This is consistent with recent proposals (Tao et al., 2014). OS-195 ($C_7H_{15}O_4S^-$), OS-249 ($C_{10}H_{17}O_5S^-$), OS-255 ($C_9H_{19}O_6S^-$), OS-267 ($C_{10}H_{19}O_6S^-$), OS-281 ($C_{10}H_{17}O_7S^-$), OS-299 ($C_{10}H_{19}O_8S^-$), OS-307 ($C_{12}H_{19}O_7S^-$) and OS-311 ($C_{10}H_{15}O_9S^-$) have been recently identified in ambient aerosol collected from the major urban locations Shanghai and Hong Kong (Tao et al., 2014; Kuang et al., 2015; Wang et al., 2015). In the absence of retention times and chromatographic conditions, OS isobars such as OS-249 or OS-279, which are currently assigned to biogenic-derived OSs (Ma et al., 2014), could also arise from anthropogenic sources such as photooxidation of cyclodecane, especially in urban areas.

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4. Conclusions

The present study demonstrates the formation of OSs from the photooxidation of alkanes and complements the smog chamber study on formation of OSs and sulfonates from photooxidation of PAHs (Riva et al., 2015a). Together, the results strongly support the importance of the contribution of anthropogenic precursors to OS in ambient urban $PM_{2.5}$ proposed on the basis of aromatic and aliphatic OSs in fine aerosol collected from several major urban locations (Kundu et al., 2013, Tao et al., 2014). Chemical characterization of OSs that were identified in SOA arising from the photooxidation of alkanes were performed and tentative structures have been proposed for OSs identified from the photooxidation of decalin, cyclodecane and docecane based on composition from exact mass measurement, DBE calculations and the transformations expected from hydroxyl radical oxidation dominated by RO_2/HO_2 chemistry. Enhancement of OS yields in the presence of acidified ammonium sulfate seed is consistent with reactive uptake of gas-phase epoxides as the pathway for OS formation. As previously proposed for IEPOX formation (Paulot et al. 2009), isomerization of RO_2 species to β hydroperoxy alky radicals followed by elimination of OH, is a plausible pathway to gas-phase epoxides. However, more work is required to validate pathway(s) leading to the formation of gaseous epoxy-products. Of critical importance would be investigations starting from authentic primary or secondary oxidation products suggested in this study as putative intermediates to validate the proposed mechanisms. A novel pathway involving reactive uptake of hydroperoxides followed by hydrolysis/sulfation reactions is proposed to explain the formation of OS-279 ($C_{12}H_{23}O_5S^-$); however, more work is also required to examine how acidified sulfate seed aerosols take up organic peroxides from the gas phase and how particle-phase reactions might degrade organic peroxides into low-volatility products such as the OSs.

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Table 1. Summary of outdoor smog chamber conditions used for the photooxidation of long-chain alkanes using isopropyl nitrite (IPN) as an OH radical precursor.

Hydrocarbons (HCs)	Initial [HC] (ppb)	Chamber Side	Seed aerosol	Initial [IPN] (ppb)	T (K)	RH (%)	Final OA mass (μg m^{-3})
Dodecane	412	N	Non-Acidified	215	304-311	49-59	58
	420	S	Acidified	212	305-311	51-63	65
Dodecane	422	N	Non-Acidified	215	302-308	15-20	49
	427	S	Acidified	212	303-308	14-17	53
Dodecane	397	N	Acidified	215	304-309	45-52	52
	409	S	Acidified	212	305-310	15-19	59
Decalin	175	N	Non-Acidified	138	302-309	48-45	204
	180	S	Acidified	136	302-308	51-49	224
Decalin	199	N	Non-Acidified	138	305-306	13-13	200
	204	S	Acidified	136	306-306	13-14	211
Decalin	N.I.	N	Acidified	138	302-306	43-54	245
	N.I.	S	Acidified	136	301-306	9-12	270
Cyclodecane	257	N	Non-Acidified	172	298-301	53-61	218
	263	S	Acidified	170	299-301	52-60	238
Cyclodecane	256	N	Non-Acidified	172	300-303	13-15	177
	261	S	Acidified	170	300-302	13-14	210
Cyclodecane	245	N	Acidified	172	298-300	10-11	259
	250	S	Acidified	170	299-300	51-49	270

N and S design "North chamber" and "South Chamber", respectively; N.I.: No Information.

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Table 2. Concentrations (ng m^{-3}) of OSs identified in laboratory-generated dodecane, decalin and cyclodecane SOA and in fine aerosol collected from two urban locations.

		Lahore, Pakistan					Pasadena, USA							
$[M-H]^-$	Precursors	04-30-2007	05-06-2007	05-12-2007	11-02-2007	11-08-2007	05-17-2010	05-18-2010	05-19-2010	05-23-2010	05-24-2010	05-25-2010	05-28-2010	06-11-2010
$C_7H_{13}O_5S^-$ (209.0472)[a,b]	Dodecane	7.53	6.53	4.24	6.35	9.66	*N.d.*	*N.d.*	0.27	0.07	0.10	*N.d.*	0.09	0.21
$C_9H_{17}O_5S^-$ (237.0786)[a,b]	Dodecane	9.35	6.81	4.27	7.27	12.40	0.13	0.15	0.30	0.10	0.16	0.16	0.13	0.25
$C_{10}H_{19}O_5S^-$ (251.0946)[a,c]	Cyclodecane	10.40	7.51	4.08	13.17	20.96	*N.d.*	*N.d.*	*N.d.*	*N.d.*	*N.d.*	*N.d.*	*N.d.*	*N.d.*
$C_{10}H_{17}O_6S^-$ (265.079)[a,c]	Cyclodecane	2.83	2.45	2.15	2.86	7.63	0.18	0.21	0.35	0.14	0.15	0.16	0.15	0.36
$C_9H_{15}O_7S^-$ (267.0554)[a,c]	Decalin	0.98	1.87	1.93	2.19	6.53	0.21	0.21	0.58	0.11	0.21	0.20	0.16	0.40
$C_9H_{17}O_7S^-$ (269.0700)[a,b]	Decalin	2.04	3.02	2.22	2.62	7.56	0.42	0.38	0.58	0.26	0.40	0.38	0.35	0.56
$C_{10}H_{15}O_7S^-$ (279.0556)[a,c]	Cyclodecane	6.38	20.25	21.97	15.06	35.93	0.14	0.21	0.54	0.10	0.19	0.21	0.20	0.29
$C_{12}H_{23}O_5S^-$ (279.1272)[c,d]	Dodecane	14.57	12.18	3.41	9.50	19.56	*N.d.*	*N.d.*	*N.d.*	*N.d.*	*N.d.*	*N.d.*	*N.d.*	*N.d.*
$C_9H_{17}O_8S^-$ (285.0651)[a,c]	Decalin	*N.d.*	0.61	*N.d.*	*N.d.*	1.44	0.20	0.09	0.21	0.05	0.08	0.09	0.03	0.17
$C_{10}H_{15}O_8S$- (295.0500)[a,c]	Decalin	*N.d.*	0.53	0.48	0.54	3.78	0.17	0.22	0.65	0.08	0.17	0.24	0.19	0.52
$C_{10}H_{17}O_8S^-$ (297.0650)[a,c]	Decalin	*N.d.*	0.78	0.92	0.69	*N.d.*	0.13	0.08	0.43	0.07	0.10	0.09	0.10	0.24
$C_{10}H_{16}NO_9S^-$ (326.0550)[a,c]	Decalin	0.25	0.32	0.21	*N.d.*	*N.d.*	*N.d.*	0.13	0.22	0.06	0.09	0.11	0.12	0.11

[a] Quantified using authentic OS (3-pinanol-2-hydrogen sulfate, $C_9H_{13}O_6S^-$), [b] OSs belonging to group 2, [c] OSs belonging to group 1, [d] quantified using octyl sulfate OS ($C_8H_{17}O_4S^-$). Different isomers for one ion have been summed; N.d.: not detected.

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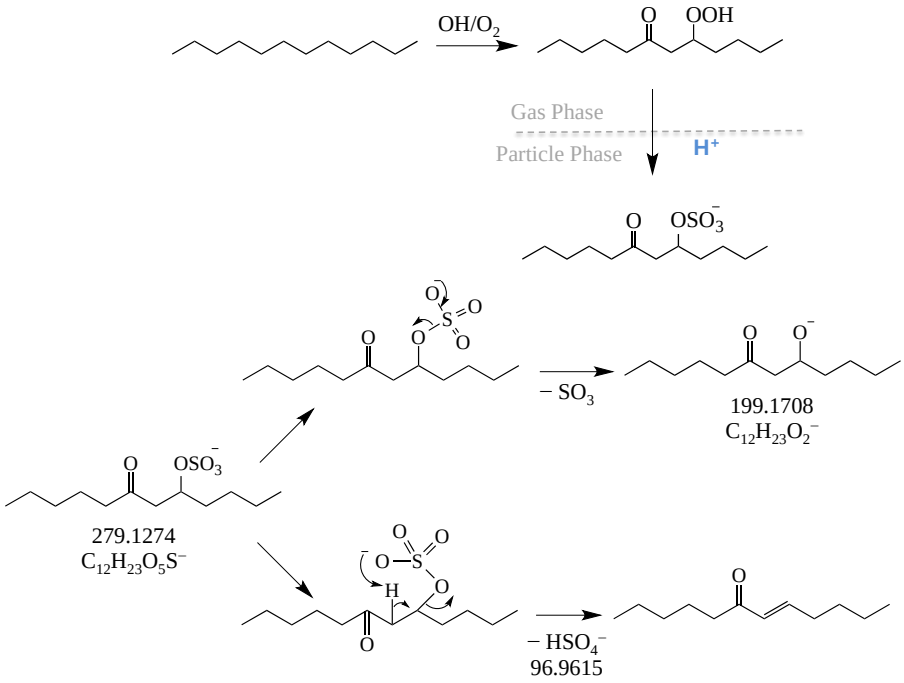

Figure 1. Proposed formation pathway of OS-279 and its corresponding fragmentation routes. The suggested mechanism is based on identified products from previous study (Yee et al., 2012).

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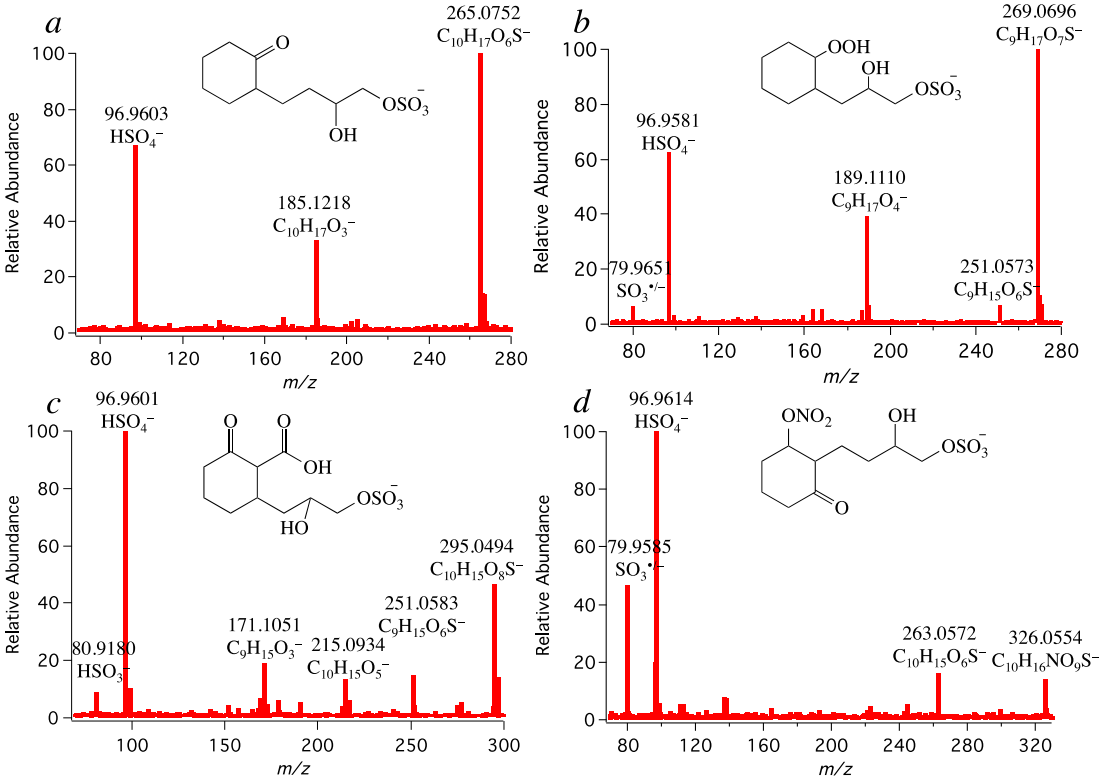

Figure 2. MS^2 spectra obtained for selected decalin-derived OSs: (*a*) *m/z* 265.0752 ($C_{10}H_{17}O_6S^-$), (*b*) *m/z* 269.0696 ($C_9H_{17}O_7S^-$), (*c*) *m/z* 295.0494 ($C_{10}H_{15}O_8S^-$) and (*d*) *m/z* 326.0554 ($C_{10}H_{16}NO_9S^-$). Fragmentation schemes are proposed in Figure S2.

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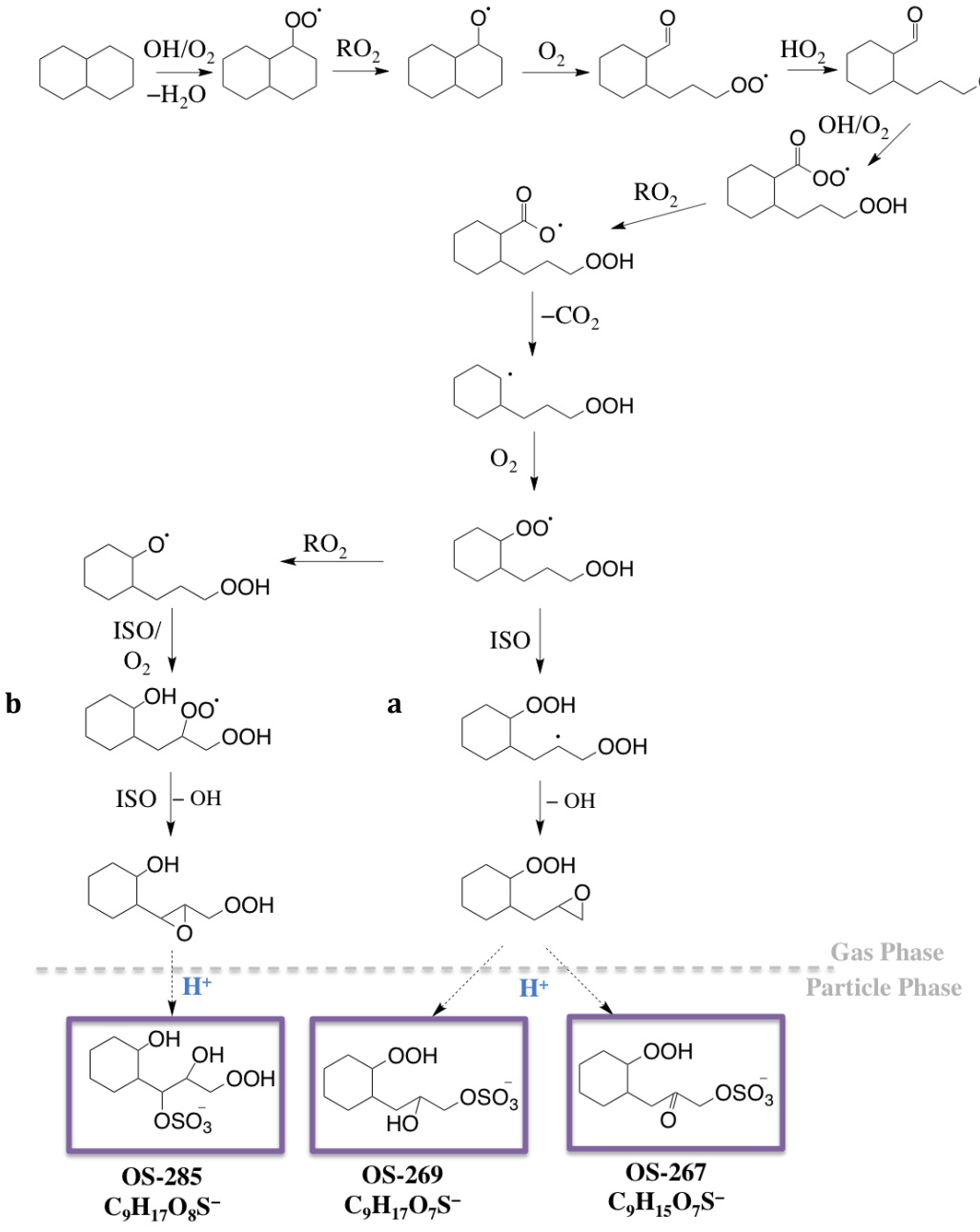

Figure 3. Proposed formation pathways of OS-267, OS-269 and OS-285 from the oxidation of decalin in presence of sulfate aerosol. ISO = isomerization reaction either through H shift (1,5- or 1,7-) or through hydeoperoxide isomerization with an R radical.

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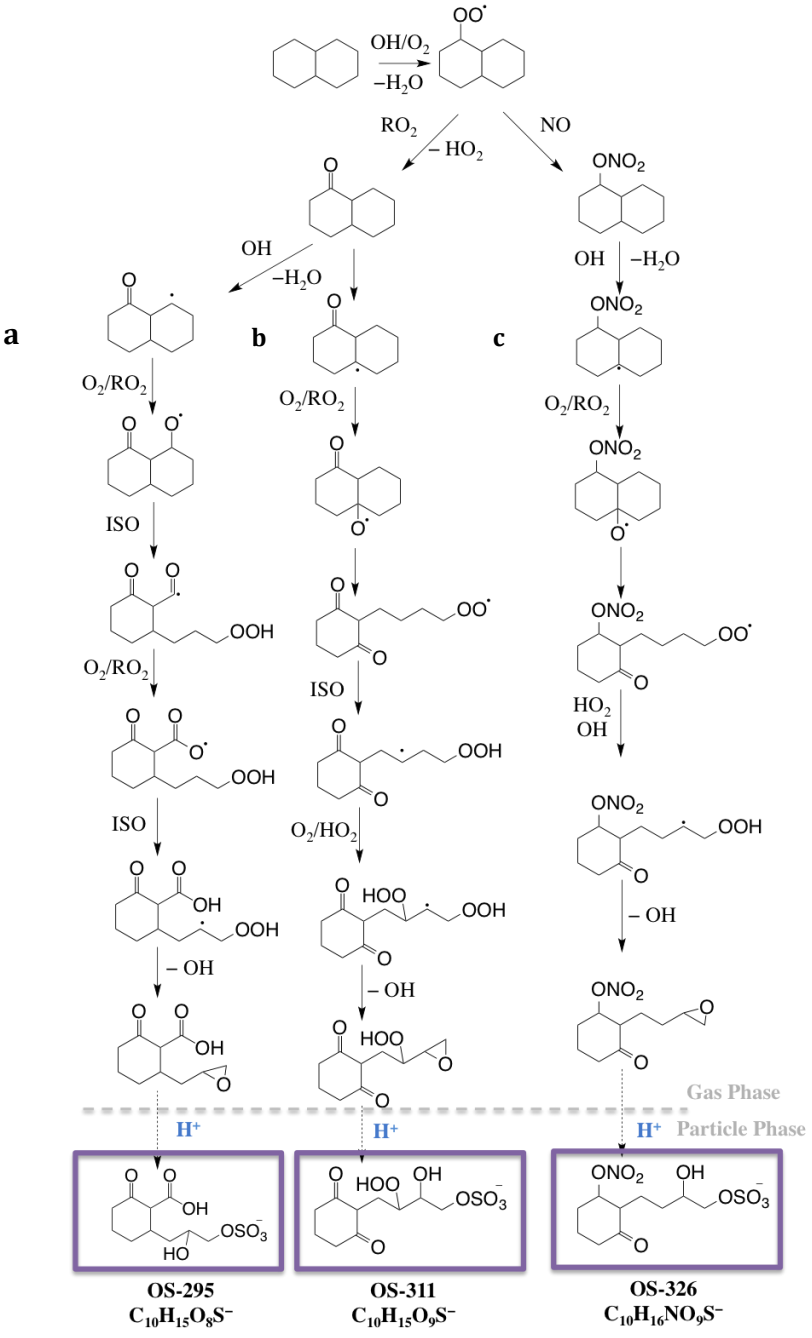

Figure 4. Proposed formation pathways of OS-295, OS-311 and OS-326 from the oxidation of decalin in the presence of sulfate aerosol. ISO = isomerization reaction either through H shift (1,5- or 1,7-) or through hydroperoxide isomerization with an R radical.

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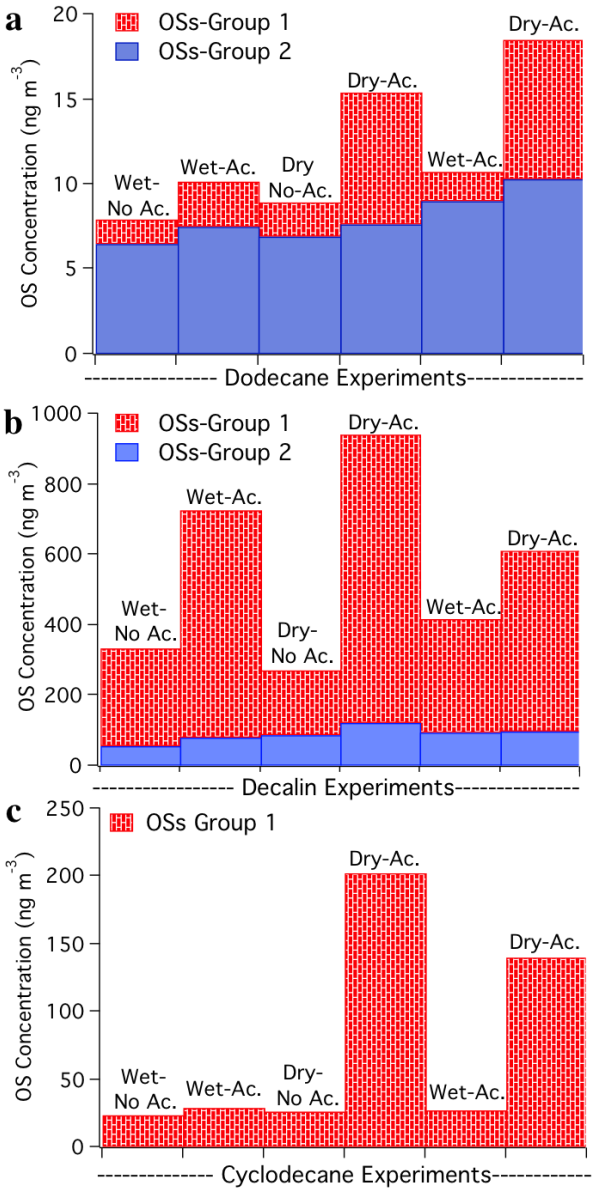

Figure 5. Impact of acidity on OS formation from gas-phase oxidation of (a) dodecane, (b) decalin, and (c) cyclodecane. OSs from Group-1 corresponds to compounds strongly impacted by aerosol acidity, while OSs from Group-2 appeared to have less dependency on aerosol acidity.

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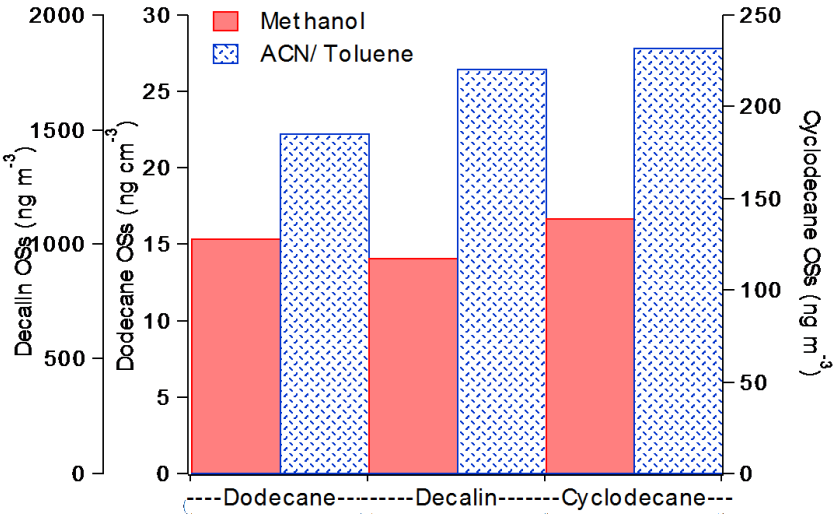

Figure 6. Impact of extraction solvent composition on quantification of identified OSs from gas-phase oxidation of alkanes.

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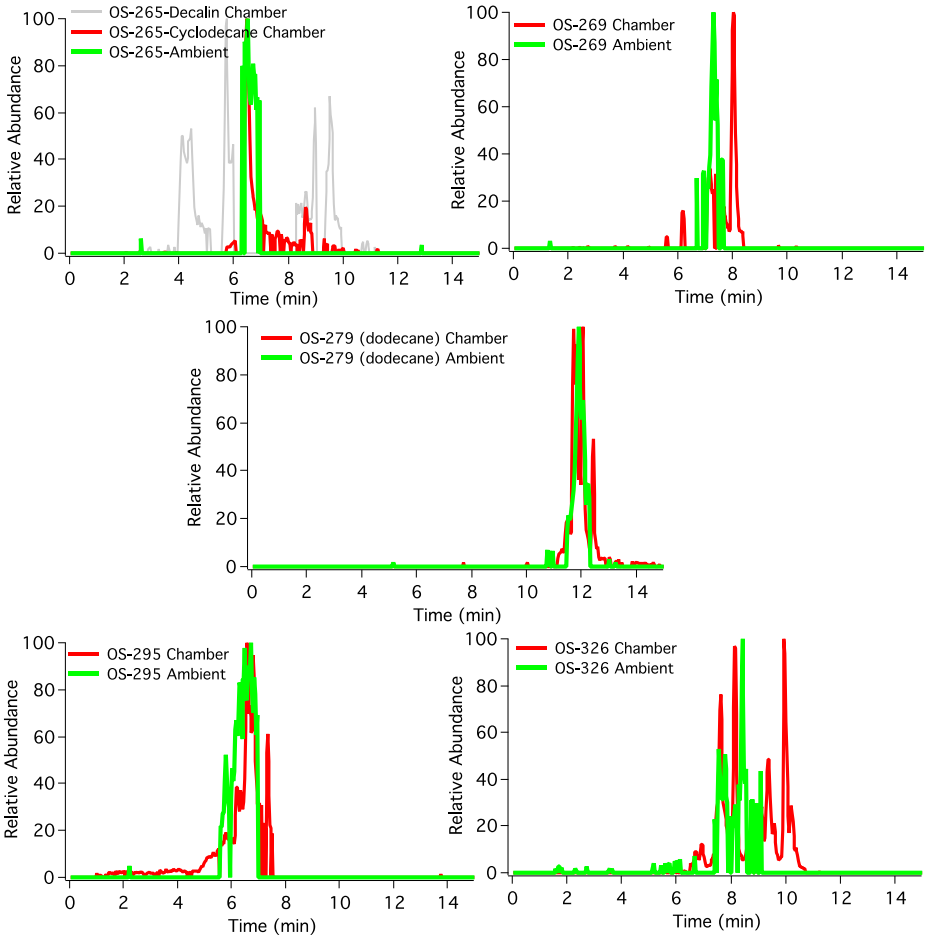

Figure 7. Extracted ion chromatograms (EICs) for selected alkane OSs identified in both smog chamber experiments (in red) and ambient samples (in green).