Chemical Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of 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 the formation of OSs from the gas-phase oxidation of anthropogenic precursors, as 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 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 and/or heterogeneous reactions of hydroperoxides. The OSs identified here were also observed and quantified in fine urban aerosol samples collected in Lahore, Pakistan, and Pasadena, CA, USA. Several 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.
1. Introduction

Atmospheric fine aerosol (PM$_{2.5}$, aerosol with aerodynamic diameter $\leq 2.5 \mu$m) 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 omission of intermediate volatility organic compounds (IVOC) as SOA precursors, such as alkanes or polycyclic aromatic hydrocarbons (PAHs), could contribute in part to the underestimation of SOA mass observed in urban areas (Robinson et al., 2007; Tkacik et al., 2012). 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; 2013), 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; Tkacik et al., 2012; 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 (Lambe et al., 2012; Carrasquillo et al., 2014; Loza et al., 2014; Hunter et al., 2014).

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 to 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; Wang et al., 2015; Kuang et al., 2016), 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 OS precursors (Tao et al., 2014; Wang et al., 2015; Kuang et al., 2016). 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; Wang et al., 2015; Kuang et al., 2016), 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 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 reduces 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 (Inuma et al., 2009). 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 (Inuma 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. These alkanes were selected based on their potential contribution to atmospheric SOA formation (Hunter et al., 2014). Studies have demonstrated that cyclic compounds (<C$_{12}$) are expected to be more efficient SOA precursors than linear or branched alkanes with the same number of carbons.
Alkanes ≥ C₅ are considered as effective SOA precursors, especially when placed in the context of their emission rates (Pye and Pauliot, 2012). Effects of RH and aerosol acidity 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 equipped with electrospray ionization (UPLC/ESI-HR-QTOFMS). In addition, effect of solvent mixture (methanol vs acetonitrile/toluene) on OS quantification was investigated. Finally, PM₂.₅ samples collected from Lahore, Pakistan and Pasadena, CA, 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–m³ dual chamber divided into two sides by a Teflon film curtain. One side referred as “North Chamber” has an actual volume of 136 m³, and the other side referred as “South Chamber” has an actual volume of 138 m³. 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 (40–60%). 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 \(\mu\)g m\(^{-3}\) in humid conditions and less than ~ 0.2 \(\mu\)g 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\(_4\))\(_2\)SO\(_4\) or 0.06 M (NH\(_4\))\(_2\)SO\(_4\) + 0.06 M H\(_2\)SO\(_4\), respectively.

After 15 min of atomization, ~ 40 \(\mu\)g m\(^{-3}\) of seed aerosol was injected into the chambers.

After stabilization of aerosol volume concentrations, Teflon blank filters were collected (47 mm diameter, 1.0 \(\mu\)m 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 source (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.

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 CA, (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). In addition, Gentner et al. (2012) have reported significant emission of long-chain alkanes during the CalNex field study.

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 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 fibers.

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 (C₈H₁₇O₄S⁻; Sigma-Aldrich) and 3-pinanol-2-hydrogen sulfate (C₉H₁₃O₆S⁻) were used as surrogate standards to quantify the identified aliphatic OSs.

2.5 Total Organic Peroxide Analysis. The total organic peroxides in the SOA were quantified using an iodometric-spectrophotometric method adapted from Docherty et al. (2005). As described in Surratt et al. (2006), the method employed in this work differs in the choice of extraction solvent: we used a 50:50 (v/v) mixture of methanol and ethyl acetate, rather than pure ethyl acetate. Calibrations and measurements were performed at 470 nm using a Hitachi U-3300 dual beam spectrophotometer. Benzoyl peroxide was used as the standard for quantification of organic peroxides formed from alkane oxidations. The molar absorptivity measured from the calibration curve was ~ 825, which is in excellent agreement with previously reported values (Docherty et al., 2005; Surratt et al., 2006).
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\(_3^−\)), 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 the low-abundance 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., 2016). Concentrations of the products are reported in Table S2. Three isobaric parent ions with \( m/z \) 279 (C\(_{12}\)H\(_{23}\)O\(_5\)S\(^−\), 279.1254), hereafter referred to as OS-279, were identified in SOA generated from dodecane oxidation in the presence of acidified ammonium sulfate aerosol. Kwok and Atkinson (1995) have reported that OH oxidation of long-chain alkane preferentially occurred at an internal carbon and thus multiple isomers may be proposed. Based on Yee et al. (2012; 2013) one isomer may be, however, assigned as 6-dodecanone-4-sulfate. 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. 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-NOx conditions, confirming the predicted RO2 – HO2 reaction pathway in the low-NOx regime. First-generation hydroperoxides (C12H26O2) can undergo further oxidation by reaction with OH to form either more highly oxidized products, such as dihydroperoxides (C12H26O4), or semi-volatile products (C12H24O) (Yee et al., 2012). In addition, hydroperoxides can be photolyzed to alkoxy radicals (RO) to form more highly oxidized products. Low-volatility products could then condense onto sulfate aerosols and undergo further heterogeneous reactions (Schilling Fahnestock et al., 2015) leading to OSs as discussed below. In our study, OH radicals were formed from IPN photolysis without additional injection of NO. Under these conditions, RO2 chemistry is dominated by RO2 + HO2 and/or RO2 + RO2 reactions as discussed by Raff and Finlayson-Pitts (2010). Although RO2 radicals could also react with NO formed by either IPN or NO2 photolysis, formation of ozone under chamber conditions (0.3-0.6 ppm, depending on the concentration of IPN injected, Table 1) would rapidly quench NO (Atkinson et al., 2000). Therefore, RO2 + NO reactions are not expected to be significant. In addition, total organic peroxide aerosol concentrations, presented in Table 1, reveal that organic peroxides account (on average) for 28 % of the SOA mass measured in the different experiments in support of a significant contribution of RO2 + RO2/HO2 and/or RO2 autoxidation to SOA formation from alkanes oxidations.

Carbonyl hydroperoxide (C12H24O3), which has been identified in the gas phase by Yee et al. (2012), is likely involved in acid-catalyzed heterogeneous reactions onto sulfate aerosol. Heterogeneous chemistry of gas-phase organic peroxides has been previously suggested to explain the formation of certain OSs and tetrols (Riva et al., 2016). 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. It should be mentioned that photooxidation of dodecane has also been investigated using an additional injection of NO (200 ppb) prior IPN injection. In this experiment SOA formation was significantly reduced as well as the OS concentrations (factor of 3-4), confirming that NO strongly impacts the formation of OSs, such as OS-279.

**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 (Lim and Ziemann, 2005; Lambe et al., 2012; Tkacik et al., 2012; Yee et al., 2013; Hunter et al., 2014; Loza 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; Wang et al., 2015; Kuang et al., 2016). MS² 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 MS² spectra and fragmentation schemes of selected parent ions at m/z 265.0752 (OS-265), 269.0696 (OS-269), 295.0494 (OS-295) and 326.0554 (OS-326). MS² 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. The different reaction
pathways presented below, are separated based on OSs that are generated from branching
reactions of a common transient. Four isomers of OS-265 with composition $\text{C}_{10}\text{H}_{17}\text{O}_6\text{S}^-$ 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 $\text{C}_{10}\text{H}_{17}\text{O}_6\text{S}^-$ 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 ($\text{HSO}_4^-$) and
loss of neutral $\text{SO}_3$ in the MS$^2$ spectrum (Figure 2a) is consistent with an aliphatic OS having
a labile proton in a $\beta$ 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
cleavage of the $\text{C}_1$−$\text{C}_2$ decalin bond, followed by reaction with a second $\text{O}_2$ molecule and HO$_2$
leads to a terminal carbonyl hydroperoxide ($\text{C}_{10}\text{H}_{18}\text{O}_3$) (Yee et al., 2013). $\text{C}_{10}\text{H}_{18}\text{O}_3$ could then
further react with OH radicals and lead to an epoxide and sulfate ester by reactive
uptake/heterogeneous chemistry (Paulot et al., 2009). OS-265 ($\text{C}_{10}\text{H}_{17}\text{O}_6\text{S}^-$) could also arise
from the acid-catalyzed perhydrolysis of the hydroperoxide ($\text{C}_{10}\text{H}_{18}\text{O}_4$) generated from the
reaction of $\text{C}_{10}\text{H}_{17}\text{O}_4^+$ + HO$_2$ (Figure S8, pathway b). The MS$^2$ spectrum for the single parent
ion at $m/z$ 281 corresponding to the composition $\text{C}_{10}\text{H}_{17}\text{O}_7\text{S}^-$ (OS-281) gave product ions
expected for a sulfate ester $\beta$ 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 a 4-(cyclohexan-2-one)but-1-yl radical followed by reaction with $\text{O}_2$ and a 1,5-H
shift (Crounse et al., 2011; Orlando and Tyndall, 2012) and lead to a $\text{C}_{10}$-carbonyl-
hydroxyhydroperoxide (C_{10}H_{18}O_{4}). C_{10}H_{18}O_{4} could then further react with OH radical and by elimination of OH lead to an epoxide (Figure S8, pathway b). In addition, OS-281 could arise from acid-catalyzed perhydrolysis of C_{10}-carbonyl dihydroperoxides (C_{10}H_{18}O_{5}) as proposed in Figure S8, pathway c. 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_{8}S^{-} 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 (Crounse et al., 2011; Orlando and Tyndall, 2012) followed by addition of a second O_{2} molecule, a 1,5-H shift and elimination of OH to yield an epoxide, which leads to a sulfate ester by reactive uptake onto acidified aerosols. The direction of ring opening of the internal alkyl epoxide is arbitrary.

The composition of the parent ion at m/z 269.0696 (C_{9}H_{17}O_{7}S^{-}) 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 satisfy the molecular formulas obtained by the accurate mass measurement. Although ESI-MS in the negative ion mode is not sensitive to multifunctional hydroperoxides and alcohols (Cech and Enke, 2001; Witkowski and Gierczak, 2012), this technique is highly sensitive to hydroperoxides and alcohols, which also contain OS groups and give [M – H]^{-} ions (Surratt et al., 2008; Kristensen et al., 2011; Kundu et al., 2013; Hansen et al., 2014).
In Figure 3, tentative pathways leading to the formation of OS-267, OS-269 and OS-285 are proposed. Under low-NOx conditions, abstraction of a proton α to the ring scission of decalin followed by reaction with O₂ leads to the 1-hydroperoxy radical, which in turn can react with another RO₂ radical to yield the corresponding alkoxy radical (C₁₀H₁₇O’) (Atkinson, 2000). Cleavage of the C₁-C₂ decalin bond, followed by reaction with a second O₂ molecule and HO₂ leads to a terminal carbonyl hydroperoxide (C₁₀H₁₆O₃) (Yee et al., 2013). The aldehydic intermediate in the sequence following C₁-C₂ ring scission may be oxidized to the corresponding acyl radical either by photolysis (Wang et al., 2006) or by H-abstraction (Kwok and Atkinson 1995) followed by addition of O₂, reaction with RO₂ or HO₂ and decarboxylation of the resulting acyl-oxy radical (R(O)O) (Chacon-Madrid et al., 2013) to a hydroperoxyperoxy radical (C₉H₁₇O₄’). C₉H₁₇O₄’ can react via pathway a (Figure 3) through a 1,6-H shift (Crounse et al., 2011; Orlando and Tyndall, 2012) followed by elimination of OH resulting in a formation of an epoxide 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 (C₉H₁₇O₅S⁻). The MS² spectrum of OS-285 (C₉H₁₇O₅S⁻; Figure S5) shows product ions corresponding to HSO₃⁻, HSO₄⁻ and loss of neutral SO₃, 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 formation of reaction of the hydroperoxyperoxy radical intermediate in pathway b with RO₂ followed by a 1,4-H shift (Rissanen et al., 2015) and addition of O₂ to give a hydroxyhydroperoxyperoxy radical (C₉H₁₇O₅’). C₉H₁₇O₅’ could then lead to an epoxide by isomerization (Inuma et al., 2009; Surratt et al., 2010; Jacobs et al., 2013; Mael et al., 2015) and form OS-285. C₉H₁₇O₅’ could also react with HO₂ and form the corresponding C₉-hydroxydihydroperoxide (C₉H₁₈O₃), which could then undergo heterogeneous reaction and lead to OS-269 (Figure 3, pathway b). Finally, a C₅-carbonyl hydroperoxide (C₅H₁₀O₃) could also be formed from the RO + O₂ reaction...
(Figure 3, pathway c), which could then further react with OH radicals and lead to a C$_9$-carbonyl dihydroperoxide (C$_9$H$_{16}$O$_2$). Hence, C$_9$H$_{16}$O$_2$ could form OS-267 (C$_9$H$_{15}$O$_7$S$^-$) from heterogeneous reaction on acidic aerosols.

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$_7$S$^-$) were identified in decalin-derived SOA under all experimental conditions. 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., 2015).

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 and further RO$_2$ isomerization (1,8-H shift) leading to a 4-(carboxy cyclohexyl)-1-hydroperoxybut-2-yl radical via RO$_2$ chemistry. Although considered as a minor reaction pathway (Crounse et al., 2013), the acyloxy radical could lead to the epoxide from the isomerization of the O$_2$ adduct (Paulot et al., 2009; Yao et al., 2014; Zhang et al., 2015). Further acid-catalyzed ring opening of the epoxide leads to OS-295 (C$_{10}$H$_{15}$O$_7$S$^-$).

Two isobaric parent ions with identical MS$^2$ spectra were observed at m/z 311 (C$_{10}$H$_{15}$O$_9$S$^-$; 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-oxy 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 H1 rather than H6 would lead to an isobaric structure.

Four isobaric ions corresponding to $\text{C}_{10}\text{H}_{16}\text{NO}_9\text{S}^-$ with analogous MS$^2$ spectra (Figure 2d) 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). Although RO$_2$ + NO reactions are expected to be minor under the conditions used in this work (i.e. NO < 1 ppb, formation of RO radicals or organonitrates cannot be ruled out. Indeed, Ehn et al. (2014) have demonstrated that NO reactions could be competitive at ppb levels. Under our experimental conditions RO$_2$ + NO, RO$_2$ + HO$_2$/RO$_2$ and RO$_2$ autoxidation are possible. Therefore, the parent ion at $m/z$ 326 could arise from the reaction of the decalin-2-peroxy radical with NO to form decalin-2-nitrate ($\text{C}_{10}\text{H}_{17}\text{NO}_3$) with subsequent reactions shown in Figure 4, pathway c. 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 OSs with the same elemental composition of $\text{C}_{10}\text{H}_{16}\text{NO}_9\text{S}^-$ isobars have also been identified in SOA produced from the gas-phase oxidation of monoterpenes (Surratt et al., 2008).

### 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 observed in the MS$^2$ spectrum suggests the presence of a terminal carbonyl or a carboxyl functional group in the cyclodecane-OSs, which is consistent with conservation of the
cyclodecane ring. 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 Figure S14 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 reacts with RO$_2$ to yield alkoxy radicals (Atkinson and Arey, 2003; Ziemann and Atkinson, 2012) or undergoes intramolecular H-shifts leading to generation of hydroperoxides (Ehn et al., 2014; Jokinen et al., 2014; Mentel et al., 2015). The formation of compounds such as cyclodecanone (C$_{10}$H$_{18}$O), cyclodecane hydroperoxide (C$_{10}$H$_{20}$O$_2$) or cyclodecane hydroxyhydroperoxide (C$_{10}$H$_{20}$O$_3$) are proposed as intermediate products leading to epoxy-compounds after additional oxidation/isomerization processes, as presented in Figure S14. In addition C$_{10}$H$_{20}$O$_3$, cyclodecane hydroperoxide ketone (C$_{10}$H$_{18}$O$_3$) and cyclodecane hydroxyoxohydroperoxide (C$_{10}$H$_{18}$O$_4$), proposed as intermediate products, could condense onto wet acidic aerosols and lead to the corresponding OSs through acid-catalyzed perhydrolysis reactions (Figure S14). 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 Figure S14 are arbitrary. Isobars may be explained by cis/trans epoxide ring opening or the span of an H-shift (1,5-/1,8-H shifts are possible) (Orlando and Tyndall, 2012). 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 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 (Inuma 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 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., 2015). Based on these observations, the formation of Group-1 OSs are hypothesized to be products of reactive uptake of gas-phase epoxides.

3.5 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 C₁₀⁻ and C₁₂⁻ OS products, including highly oxidized OS, appear more efficiently extracted by the ACN/toluene mixture. For OSs smaller than C₁₀, 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; Inuma 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 > C₁₀.

3.6 OSs Derived from Alkanes in Ambient Fine Urban Aerosol. Archived fine urban aerosol samples collected at Lahore, Pakistan, and Pasadena, CA, USA were used to evaluate and quantify OSs identified in SOA produced from the photooxidation of 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 S15
Table 2 identifies 12 OSs, along with concentrations, present in PM$_{2.5}$ collected from Lahore, Pakistan and Pasadena, CA, 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 of alkanes in urban areas. This is consistent with recent proposals (Tao et al., 2014). OS-195 (C$_{7}$H$_{15}$O$_{4}$S$^-$), OS-249 (C$_{10}$H$_{17}$O$_{6}$S$^-$), OS-255 (C$_{9}$H$_{19}$O$_{6}$S$^-$), OS-267 (C$_{10}$H$_{19}$O$_{6}$S$^-$), OS-281 (C$_{10}$H$_{17}$O$_{7}$S$^-$), OS-299 (C$_{10}$H$_{19}$O$_{8}$S$^-$), OS-307 (C$_{12}$H$_{19}$O$_{7}$S$^-$) and OS-311 (C$_{10}$H$_{15}$O$_{9}$S$^-$) have been recently identified in ambient aerosol collected from the major urban locations Shanghai and Hong Kong (Tao et al., 2014; Wang et al., 2015; Kuang et al., 2016). 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.

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., 2015). 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 dodecane 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 alkyl 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, since OS formation from other chemical pathways such as nucleophilic substitution of the –ONO$_2$ group by a –OSO$_3$ group cannot be ruled out (Darer et al., 2011; Hu et al., 2011). 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 heterogeneous reactions of hydroperoxides followed by hydrolysis/sulfation reactions is proposed to explain the formation of 8 OSs identified in this study; 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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References


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.

<table>
<thead>
<tr>
<th>Hydrocarbons (HCs)</th>
<th>Initial [HC] (ppb)</th>
<th>Chamber Side</th>
<th>Seed aerosol</th>
<th>Initial [IPN] (ppb)</th>
<th>[NO] (ppb)</th>
<th>[O₃] (ppb)</th>
<th>T (K)</th>
<th>RH (%)</th>
<th>Final OA mass (μg m⁻³)</th>
<th>Total Peroxides (μg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>412</td>
<td>N</td>
<td>Non-Acidified</td>
<td>215</td>
<td>&lt; 1</td>
<td>512</td>
<td>304-311</td>
<td>49-59</td>
<td>58</td>
<td>N.d.</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>S</td>
<td>Acidified</td>
<td>212</td>
<td>&lt; 1</td>
<td>528</td>
<td>305-311</td>
<td>51-63</td>
<td>65</td>
<td>N.d.</td>
</tr>
<tr>
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<td>N</td>
<td>Non-Acidified</td>
<td>215</td>
<td>&lt; 1</td>
<td>507</td>
<td>302-308</td>
<td>15-20</td>
<td>49</td>
<td>N.d.</td>
</tr>
<tr>
<td></td>
<td>427</td>
<td>S</td>
<td>Acidified</td>
<td>212</td>
<td>&lt; 1</td>
<td>538</td>
<td>303-308</td>
<td>14-17</td>
<td>53</td>
<td>N.d.</td>
</tr>
<tr>
<td>Dodecane</td>
<td>397</td>
<td>N</td>
<td>Acidified</td>
<td>215</td>
<td>&lt; 1</td>
<td>506</td>
<td>304-309</td>
<td>45-52</td>
<td>52</td>
<td>15.4</td>
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<td>409</td>
<td>S</td>
<td>Acidified</td>
<td>212</td>
<td>&lt; 1</td>
<td>585</td>
<td>305-310</td>
<td>15-19</td>
<td>59</td>
<td>15.2</td>
</tr>
<tr>
<td>Decalin</td>
<td>175</td>
<td>N</td>
<td>Non-Acidified</td>
<td>138</td>
<td>&lt; 1</td>
<td>327</td>
<td>302-309</td>
<td>48-45</td>
<td>204</td>
<td>N.d.</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>S</td>
<td>Acidified</td>
<td>136</td>
<td>&lt; 1</td>
<td>335</td>
<td>302-308</td>
<td>51-49</td>
<td>224</td>
<td>N.d.</td>
</tr>
<tr>
<td>Decalin</td>
<td>199</td>
<td>N</td>
<td>Non-Acidified</td>
<td>138</td>
<td>&lt; 1</td>
<td>317</td>
<td>305-306</td>
<td>13-13</td>
<td>200</td>
<td>59.7</td>
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<tr>
<td></td>
<td>204</td>
<td>S</td>
<td>Acidified</td>
<td>136</td>
<td>&lt; 1</td>
<td>328</td>
<td>306-306</td>
<td>13-14</td>
<td>211</td>
<td>75.5</td>
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<tr>
<td>Decalin</td>
<td>N.I.</td>
<td>N</td>
<td>Acidified</td>
<td>136</td>
<td>&lt; 1</td>
<td>319</td>
<td>302-306</td>
<td>43-54</td>
<td>245</td>
<td>43.9</td>
</tr>
<tr>
<td>Decalin</td>
<td>N.I.</td>
<td>S</td>
<td>Acidified</td>
<td>136</td>
<td>&lt; 1</td>
<td>324</td>
<td>301-306</td>
<td>9-12</td>
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<td>57.8</td>
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<tr>
<td>Cyclodecane</td>
<td>257</td>
<td>N</td>
<td>Non-Acidified</td>
<td>172</td>
<td>&lt; 1</td>
<td>374</td>
<td>298-301</td>
<td>53-61</td>
<td>218</td>
<td>76.6</td>
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<tr>
<td></td>
<td>263</td>
<td>S</td>
<td>Acidified</td>
<td>170</td>
<td>&lt; 1</td>
<td>364</td>
<td>299-301</td>
<td>52-60</td>
<td>238</td>
<td>72.2</td>
</tr>
<tr>
<td>Cyclodecane</td>
<td>256</td>
<td>N</td>
<td>Non-Acidified</td>
<td>172</td>
<td>&lt; 1</td>
<td>350</td>
<td>300-303</td>
<td>13-15</td>
<td>177</td>
<td>57.8</td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>S</td>
<td>Acidified</td>
<td>170</td>
<td>&lt; 1</td>
<td>332</td>
<td>300-302</td>
<td>13-14</td>
<td>210</td>
<td>68.3</td>
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<tr>
<td>Cyclodecane</td>
<td>245</td>
<td>N</td>
<td>Acidified</td>
<td>172</td>
<td>&lt; 1</td>
<td>345</td>
<td>298-300</td>
<td>10-11</td>
<td>259</td>
<td>78.8</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>S</td>
<td>Acidified</td>
<td>170</td>
<td>&lt; 1</td>
<td>355</td>
<td>299-300</td>
<td>51-49</td>
<td>270</td>
<td>69.2</td>
</tr>
</tbody>
</table>

N and S design “North chamber” and “South Chamber”, respectively; N.I.: No Information, N.d. Not determined
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.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Lahore, Pakistan</th>
<th>Pasadena, USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (209.0472)$^{ab}$</td>
<td>Dodecane</td>
<td>7.53</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (237.0786)$^{ab}$</td>
<td>Dodecane</td>
<td>9.35</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (251.0946)$^{ac}$</td>
<td>Cyclodecane</td>
<td>10.40</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (265.079)$^{ac}$</td>
<td>Cyclodecane</td>
<td>2.83</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (269.0700)$^{ab}$</td>
<td>Decalin</td>
<td>0.98</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (269.0700)$^{ab}$</td>
<td>Decalin</td>
<td>2.04</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (279.0556)$^{ac}$</td>
<td>Cyclodecane</td>
<td>6.38</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (279.0556)$^{ac}$</td>
<td>Dodecane</td>
<td>14.57</td>
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<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (285.0651)$^{ac}$</td>
<td>Decalin</td>
<td>N.d.</td>
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<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (295.0500)$^{ac}$</td>
<td>Decalin</td>
<td>N.d.</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$O$_{5}$S$^{-}$ (297.0650)$^{ac}$</td>
<td>Decalin</td>
<td>N.d.</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{17}$NO$_{5}$S$^{-}$ (326.0550)$^{ac}$</td>
<td>Decalin</td>
<td>0.25</td>
</tr>
</tbody>
</table>

$^{a}$Quantified using authentic OS (3-pinanol-2-hydrogen sulfate, C$_{9}$H$_{13}$O$_{6}$S$^{-}$), $^{b}$OSs belonging to group 2, $^{c}$OSs belonging to group 1, $^{d}$quantified using octyl sulfate OS (C$_{8}$H$_{17}$O$_{4}$S$^{-}$). Different isomers for one ion have been summed; N.d.: not detected.
Figure 1. Proposed formation pathway of OS-279 ($m/z$ 279.1274) and its corresponding fragmentation routes. The suggested mechanism is based on identified products from previous study (Yee et al., 2012).
Figure 2. MS² spectra obtained for selected decalin-derived OSs: (a) m/z 265.0752 (C₁₀H₁₅O₄S⁻), (b) m/z 269.0696 (C₉H₁₇O₄S⁻), (c) m/z 295.0494 (C₁₀H₁₅O₄S⁻) and (d) m/z 326.0554 (C₁₀H₁₆NO₄S⁻). Fragmentation schemes are proposed in Figure S2.
Figure 3. Tentatively proposed formation pathways of OS-267 (m/z 267.9552), OS-269 (m/z 269.0696) and OS-285 (285.0654) from the oxidation of decalin in presence of sulfate aerosol.
Figure 4. Tentatively proposed formation pathways of OS-295 (295.0494), OS-311 (m/z 311.0447) and OS-326 (326.0554) from the oxidation of decalin in the presence of sulfate aerosol.
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.
Figure 6. Impact of extraction solvent composition on quantification of identified OSs from gas-phase oxidation of alkanes.
Figure 7. Extracted ion chromatograms (EICs) for selected alkane OSs identified in both smog chamber experiments (in red) and ambient samples (in green).