Response to Anonymous Referee #1

Interactive comment on “Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of Long-Chain Alkanes” by M. Riva et al.

Received and published: 18 February 2016

This is an interesting study about the formation of organosulfates from the oxidation of aliphatic alkanes. As the authors point out in the manuscript, earlier studies mostly pre- sented the formation of organosulfates from the oxidation of biogenic VOCs (isoprene, monoterpenes, and sesquiterpenes) or anthropogenic aromatic hydrocarbons, and this is one of the first studies to report the aliphatic alkane organosulfates. The authors conducted a series of well-designed chamber experiments, and filter sample analysis to elucidate the formation mechanisms and the structures of these organosulfates. While tandem MS experiments may not provide conclusive evidence for the structures, proposed formation mechanisms and resulting organosulfate structures are consistent with our current knowledge about atmospheric organosulfate formation pathways. In addition, the authors support the importance of the aliphatic alkane organosulfates by providing evidence for their presence in ambient PM filter samples. The manuscript is concise and very well written. I suggest the manuscript be published as is.

We thank Referee # 1 for careful consideration of our article.

Response to Anonymous Referee #2

We thank Referee # 2 for the comments and address each below. Our responses are denoted in blue texts.

Interactive comment on “Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of Long-Chain Alkanes” by M. Riva et al.

Anonymous Referee #2
Received and published: 21 February 2016

General Comments
In this manuscript the authors report results of an experimental study of the formation of organosulfates in secondary organic aerosol (SOA) formed from photochemical reactions of three alkanes: decane, dodecane, and decalin, conducted in an outdoor smog chamber. The SOA was collected on filters and analyzed using liquid chromatography- mass spectrometry to determine elemental formulas for organosulfates and to quantify the compounds. Products observed in experiments were also observed in samples collected in Pakistan and Pasadena, indicating that they can be used as tracers for SOA formation from these alkanes in ambient air. The study is technically well done and the paper is well written. I think it will eventually be suitable for publication in ACP, but I have a number of comments that should first be addressed. Most importantly, I think the proposed reaction mechanisms for forming the identified organosulfate products are highly implausible, and that other mechanisms are much more likely.

Specific Comments

1. Lines 58-60: I am not aware that it is known that the primary source of SOA model-measurement discrepancies is IVOCs. I consider this to be an ongoing debate, and that there are other sources, such as the effects of vapor wall loss on measured SOA yields, effects of multiphase chemistry, and others. The authors seem to have picked a couple references to support their particular view.

We agree that it is an ongoing debate to explain the discrepancies between the mass of SOA observed in the atmosphere and the one estimated by the different models. IVOCs have not been traditionally included in chemical transport models and it is this what we wanted to underline. To avoid confusion, we have changed the sentence as follows on lines 59-62:

"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)."

2. Lines 115-118: Why were these compounds chosen? Decane makes sense based on potential abundance, but what about decalin and dodecane? The latter two are interesting from a structural point of view, but I was under the impression that this study was interested in compounds likely to contribute significantly to ambient SOA formation. A little more discussion of the choice of these compounds is warranted.

These compounds have been selected due to their potential contribution to SOA formation in the atmosphere. Recent studies have investigated the SOA formation from decalin and dodecane oxidations and reported large SOA yields (Yee et al., 2013; Hunter et al., 2014). Moreover, Pye and Pauliot (2012) have shown that, even though less emitted into the atmosphere, the cyclic C_{10} alkanes have a greater potential for SOA formation than linear or branched alkanes $< C_{12}$.

A few sentences have been added to better explain our selection of parent VOCs on lines 118-124:

"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 (Lim and Ziemann, 2005; Pye and Pauliot, 2012). Alkanes $\geq C_{10}$ are considered as effective SOA precursors, especially when placed in the context of their emission rates (Pye and Pauliot, 2012)."

3. Line 126: Experimental. Were any blank chamber experiments conducted to determine the effect of background air components on SOA formation?

As already described in the experimental section on lines 151-155, blank filters were collected before each experiment and analyzed following the protocol described in the article to characterize organosulfate (OS) composition. None of the identified OSs was observed in the blanks collected prior to each experiment. It is important to point out that the chambers were cleaned using a clean air generator for at least few hours and the concentration of VOCs are expected to be the same background level as NO_x and O_3 (few ppb). Most importantly, due to the concentration of SOA precursors used in this work (> 150-200 ppb) the impact of VOCs present in the background could be considered negligible. Moreover, we did not observe any SOA constituents other than those derived from alkanes used in the chamber experiments.

4. Were background VOCs identified/quantified?

Gas-phase samples were collected before and during each experiment using GC-FID. As explained in the previous comment, the impact of any background VOCs could be considered negligible; especially since OA constituents were not observed from chamber filter blanks (filters collected from the flushed chamber).

5. Line 226-230: The authors have mistakenly assumed that the results of a condensed phase oxidation study can be applied to the gas phase. Ruehl et al. observed enhanced OH reaction at the ends of alkane molecules in drops because of the orientation of the molecules with respect to the liquid surface. In the gas phase no such preference occurs, as that study also showed. In fact, it is well established that the primary H atoms on terminal carbons are about 10 times less reactive with OH radicals than the secondary H atoms on internal carbon atoms (Kwok and Atkinson, Atmos. Environ. (1995), 29, 1685-1695). Reaction occurs preferentially on internal carbons.

We agree with the reviewer 2 and we have removed this sentence.

6. Line 239-240: Raff and Finlayson-Pitts do not show that RO_2-RO_2 chemistry dominates in isopropyl nitrite photolysis, only that it contributes to the chemistry. Because NO_2 is photolyzed in these systems NO is recycled and so available for reaction with RO_2 radicals, even when O_3 is present.

We did not mention that RO_2 chemistry is dominated by RO_2 + RO_2 reactions as it seems to be stipulated by referee #2. As it is underlined in Raff and Finlayson-Pitts *"without additional NO injection, the yields drop to 0.70 ± 0.01 and 0.58 ± 0.03, respectively. The dramatic* *differences in product yields likely reflect differences in RO_2 + HO_2 and RO_2 + RO_2 pathways favored in the low-NOx situation versus the RO_2 + NO pathways that dominate under high-NO_x conditions"*. Thus, this previous study revealed that without additional injection of NO, RO_2 chemistry could be considered as low-NO_x, as already stipulated on lines 256-257.

In our experiment we did not add NO (prior to IPN injection) and background NO levels were measured near the detection limit of the NO_x monitor (i.e., 1 ppb). After IPN injection an significant increase of O_3 was observed in all experiments (as described lines 258-260) and NO concentration dropped below 1 ppb. We agree that NO_2 is photolyzed in these systems and NO is recycled. However, under the conditions described here (and in the article on lines 258-260 and in Table 1) most of the NO is expected to react with O_3. Rate constants for the RO_2 + NO and NO + O_3 reactions were determined to be 4.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (k_1) (suggested by MCM; Ehn et al., 2014) and 1.8×10^{-14} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2000; IUPAC) (k_2), respectively. Gratien et al. (2010, ES&T, 44, 8150-8155) have calculated the OH radical concentration to be 5×10^6 molecule cm^{-3} from the photolysis of 5 ppm of isopropyl nitrite (IPN). In our experiments, 0.1-0.25 ppm of IPN was injected into the chambers. Using similar OH radical concentration to Gratien et al. (2010, ES&T) as an upper limit, RO_2 concentration could be estimated to be at the ppt level. Therefore, under the conditions of our study and assuming an O_3 concentration of 0.5 ppm, NO would react primarily with O_3: $(k_2[O_3]\,[NO])/(k_1[RO_2]\,[NO]) > 350$.

Lines 258-260 have been changed to:

"Although RO_2 radicals could also react with NO formed by either IPN or NO_2 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, RO_2 + NO reactions are not expected to be significant."

7. My major criticism of this paper is that the proposed mechanisms for forming organosulfates with the same elemental composition as the observed products are highly implausible. The authors have ignored much of what is known about the rates of competing reaction pathways and assumed that because under some set of conditions a certain reaction can occur, that it is plausible for the conditions of these experiments. In doing so, it is assumed that essentially all reactions are possible here, ranging from auto-oxidation (which requires pristine conditions), to RO2-RO2 reactions (which require low NO and high VOC

concentrations), to RO2-HO2 reactions (which require low NO and low VOC concentrations), to RO2- NO reactions (which require high NO concentrations. The authors do not present any information on the conditions with regards to NO, NO_2, O_3, etc., and so no constraints are placed on the proposed mechanisms. Regardless, it is difficult to believe that all these conditions were encountered in these experiments.

We have considered the rates of competing reaction pathways and respectfully disagree with reviewer 2. First, as demonstrated by Ehn et al. (2014), at ppb levels of NO (1-5 ppb) a competition exists between RO_2 + NO, RO_2 + HO_2 and RO_2 autoxidation reactions. Indeed, as presented in the Ehn study, ELVOC, even though reduced, still formed at NO concentrations greater than a few ppb and underlines that auto-oxidation does not occur solely under pristine conditions. In other words, different RO_2 termination pathways could compete under specific conditions. It is important to point out that the concentrations of VOCs used in this work could lead to RO_2 + RO_2 chemistry.

In order to give more evidence of our tentatively proposed mechanisms, total peroxide measurements have been performed and added to our study. These results, which are now reported in Table 1, reveal that organic peroxides contribute to ~ 28 % (on average) of the SOA mass formed from the photooxidation of the studied alkanes. These measurements highlight the significant presence of peroxides in aerosol and add support to the proposed mechanisms. In addition to the peroxide measurements, concentrations of O_3 and NO were also added in Table 1 to support the low-NO conditions observed in this work. It should be pointed out that based on the GC-FID measurements ~ 85-90% of the VOC remained present when the concentration of NO dropped below the detection limit.

In addition, Crounse et al. (2013) (reference provided by Referee #2) have also shown that RO_2 autooxidation and formation of hydroperoxides occurred in experiments using methyl nitrite, similar to IPN, as an OH radical source.

Finally, we would like to stress to this reviewer that the analytical work and interpretation of the MS^2 spectra were not questioned by any of the 3 reviewers. The tandem MS data support the proposed structures. However, we have stated in many places throughout the text that the reaction pathways are tentatively proposed and until authentic standards become available these products remain tentatively identified. The main emphasis of our paper is that aliphatic organosulfates do form from alkane oxidation, and likely offer one explanation as to why many groups have reported aliphatic OSs in urban areas (Ma et al., 2014; Tao et al., 2014)

A few sentences have been added to the revised manuscript to discuss the RO_2 chemistry on lines 404-406*:*
"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."

A description of the organic peroxide measurements been added to the manuscript on lines 211-219:
*"**Total Organic Peroxide Analysis.** The total amount of organic peroxides in the SOA was 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 slightly 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)."*

A description of the organic peroxide results has been added on lines 261-265:
"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 RO_2 + RO_2/HO_2 and/or RO_2 autoxidation to SOA formation from alkane oxidations."

Besides the problems outlined above, I have listed a few more detailed aspects of the mechanisms that are problematic.

Figure 3, Pathway A. The proposed RO_2 isomerization is much too slow to compete with other pathways (RO2, HO2, and NO reactions). See Crounse et al., J. Phys. Chem. Lett. (2013), 4, 3513-3520.

It is important to mention that we do not claim that the proposed mechanisms represent the major reaction pathways of the photooxidation of the studied alkanes, but are tentatively proposed to explain the formation of the OSs identified in this work. Indeed, concentrations reported in Tables S1-S3 underline that identified compounds are in low abundance regardless of the mass of SOA measured in all experiments. In the figure captions of each mechanism, we have added explicit statements that these are "tentatively proposed" mechanisms.

It is not clear how referee 2 could use the cited reference to point out that RO_2 isomerization is "much too slow to compete with other pathways". Here are listed some conclusions of the cited reference (the authors have calculated that "*the reactivity of* RO_2 *was 0.005* s^{-1} *with NO and 0.006* s^{-1} *with* HO_2" under the conditions of this study):

- "*Importantly, there is no evidence for the formation of* C_5*-hydroxy carbonyl nitrate (Scheme 2, HCN) or* C_5*-hydroxy carbonyl hydroperoxide (Scheme 2, HHPC). This indicates that the second H-shift involving the transfer of a H-atom α to a hydroperoxide group (Scheme 1) or a hydroxy group (Scheme 2) is at least 10 times faster than the competing reactions with NO or* HO_2 *(i.e., >0.1 s−1).*"

- "*It appears that 1,4- (aldehydic H), 1,5-, 1,6-, 1,7-, and 1,8-H-shifts to peroxy radicals (as well as intermolecular H-shifts in the condensed phase) may all be important in the oxidation of organic species in the environment and deserving of additional study.* "

- "*Examining Table 2, it is clear that for many oxygenated hydrocarbons, autoxidation will be competitive with other peroxy radical chemistry.*"

As mentioned by Crounse et al. 2013, 1,4-H – 1.8H shift may all be important in the oxidation of organic species and in Figure 3, pathway **a** proposed a 1,6-H shift suggests that this reaction pathway could occur. Recent studies from Rissanen et al. (2014; 2015) have also reported that 1,4 – 1.8-H shift reactions could contribute in formation of highly oxidized products.

Figure 3, Pathway B. The proposed RO2 isomerization through a 5-member ring, if even possible, would be much too slow to compete with isomerization through a 6- member ring to abstract a tertiary H-atom from the ring, though even this is much too slow to compete with other pathways (RO2, HO2, and NO reactions). See Crounse et al.

Formation of OS-285 (Pathway B, Figure 3) is not explained by RO_2 isomerization (even though as discussed by Crounse et al., isomerization through a 5-member ring may be important) but from RO (formed from RO_2 + RO_2 reaction) isomerization through a 1,4-H-shift (Rissanen et al., 2014, 2015).

One sentence has been added on lines 363-370:

"The structure proposed for OS-285 is based on the formation of reaction of the hydroperoxyperoxyl radical intermediate in pathway ***b*** *with RO_2 followed by a 1,4-H shift (Rissanen et al., 2015) and addition of O_2 to give a hydroxyhydroperoxyperoxyl radical ($C_9H_{17}O_5^\bullet$). $C_9H_{17}O_5^\bullet$ could then lead to an epoxide by isomerization (Iinuma et al., 2009; Surratt et al., 2010; Jacobs et al., 2013; Mael et al., 2015) and form OS-285. $C_9H_{17}O_5^\bullet$ could also react with HO_2 and form the corresponding C_9-hydroxydihydroperoxide ($C_9H_{18}O_5$), which could then undergo heterogeneous reaction and lead to OS-269 (Figure 3, pathway* ***b****)."*

Figure 4, Pathway A. The proposed RC(O)O isomerization is much too slow (by about a factor of 106) to compete with decomposition to R + CO2. See Vereecken and Peeters, PCCP (2009), 11, 9062-9074; PCCP (2010), 12, 12608-12620.

We agree that CO_2 elimination is likely the dominant pathway as it was suggested by previous work. However, similar reaction pathways have been proposed in recent studies (Yao et al., 2014; Sato et al., 2015; Zhang et al., 2015), suggesting that, even though not dominant, isomerization of acyloxy radical could occur.

We do not claim that that the tentatively proposed mechanisms represent the dominant reaction pathways from alkane photooxidation, but likely explain the formation of OSs identified in this work. All mechanisms are based on known gas-phase reactions, which have been proposed in previous studies.

One sentence has been added on lines 382-388*:*

"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 ($C_{10}H_{15}O_8S^-$).”

Figure 4, Pathway B. The proposed RO2 isomerization is much too slow to compete with other pathways (RO2, HO2, and NO reactions). See Crounse et al. It is also not clear how the alkyl radical site adjacent to the –OOH group is formed.

As discussed previously it is not clear how the referee could use Crounse et al. to argue that proposed isomerization pathways is “much too slow”.

An error was made in the mechanism and it has been corrected in the new version. Two 1,6 and 1,5-H-shift reactions lead to epoxide proposed in Figure 4. As mentioned by Crounse et al. (2013) the intramolecular barrier for H-shift to the RO_2 is minimal for 1,5- or 1,6-H-shift reactions.

Figure 4, Pathway C. Reaction involves three H-atom abstractions by OH radicals, the last two of which must occur at specific H-atoms, and with the last one occurring for a compound that would be expected to be in the particle phase where such reactions are negligibly slow.

We agree with reviewer that such oxidation processes are expected to be slow in particle phase. However, we would like to point out that it has been previously reported that highly oxidized multifunctional compounds were identified in the gas phase (Ehn et al., 2014; Rissanen et al., 2014; 2015). Therefore, gas-phase oxidation of $C_{10}H_{17}NO_6$, even though minor, could occur, leading to OS-326, which has been quantified in low abundance in the decalin-derived SOA.

These pathways are not only implausible, but if they did occur then there should be many other products that are much more likely to be present. If the authors insist on sticking with these mechanisms, then they should also address this issue. When presenting this kind of analysis it is not enough to show that there is a mechanism that could possibly explain the products, but also that other products predicted by such a mechanism are also present.

It is not clear how the referee #2 could conclude by using reference (Crounse et al., 2013) that the proposed pathways are “implausible”. Indeed this cited reference highlights “*that 1,4-(aldehydic H), 1,5-, 1,6-, 1,7-, and 1,8-H-shifts to peroxy radicals (as well as intermolecular*

H-shifts in the condensed phase) may all be important in the oxidation of organic species in the environment and deserving of additional study." Moreover, similar reaction pathways have been recently proposed from the oxidation of different VOCs and the reaction mechanisms proposed in this study are consistent with the previous studies.

It is important to point out again that, we do not argue that the proposed mechanisms represent the major pathways of photooxidation of the studied alkanes. If it was the case, the OSs identified in this work will represent most of the SOA mass measured during the different experiments, which is not the case. It should be pointed out that analyses are still ongoing to identify non-OSs reaction products in both gas and particle phases, but the main focus of this article is on the chemical characterization of OSs. Liquid chromatography coupled with electrospray ionization mass spectrometry is not a sensitive technique for detection of the intermediate reaction products proposed in the mechanisms (e.g. ketone, epoxide). As demonstrated previously, epoxides quickly react in the presence of acidified particles and are not observed in SOA (Minerath et al., 2009; Surratt et al., 2010; Mael et al., 2015). Hence, it appears difficult with the techniques used in this work to identify the primary/secondary products proposed in the mechanisms. As mentioned in the conclusion on lines 527-528 "*more work is required to validate pathway(s) leading to the formation of gaseous epoxy-products*".

In my opinion, a much more plausible mechanism for explaining these products is that a series of compounds containing C–OH, C=O, and C–ONO2 groups were formed from well-established reactions of alkanes with OH radicals under high NO conditions, and that the sulfates were formed by nucleophilic substitution of the –ONO2 group by a –OSO3 group, a reaction that is known to occur in particles.

We can't rule out potential nucleophilic substitution of the –ONO2 group by a –OSO3 group as proposed in previous work (Darer et al., 2011; Hu et al., 2011). However, gas-phase chemistry cannot explain formation of identified compounds only by C–OH, C=O, and C–ONO2 groups. As discussed above, organic peroxide compounds represent 28 % (on average) of the SOA mass, which supports the proposed alternative mechanisms.

One sentence has been added in the conclusion, lines 527-530:

"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 nuclophilic

substitution of the –ONO2 group by a –OSO3 group cannot be ruled out (Darer et al., 2011; Hu et al., 2011).”

One simple test for the mechanisms proposed by the authors is to conduct an experiment with added NO, such that the NO concentration remains significant throughout the experiment. Under these conditions no organosulfates should be formed, since the presence of NO will prevent the formation of hydroperoxides, which are proposed precursors to organosulfate formation. However, if the organosulfates observed in the original experiments were formed through the suggested high NO chemistry, then the addition of NO will have no effect.

Photooxidation of dodecane has been investigated using an additional injection of NO (200 ppb) prior to IPN injection. NO concentration dropped below ppb levels in less than 1 hour and OS concentrations were significantly reduced (factor of 3-4) compared to other experiments, underlying that NO concentration does have an impact on OS formation.

One sentence has been added to discuss the findings of this experiment, lines 274-277:

“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 OS, such as OS-279.”

Technical Comments None.

Response to Anonymous Referee #3

We thank Referee # 3 for the comments and address each below. Our responses are denoted in blue texts.

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

Reviewer's Summary:

The authors characterize organosulfates (OSs) from the laboratory oxidation of dodecane, decalin, and cyclodecane under varying conditions of humidity and two different seed types (non-acidified, acidified). They observe overlapping organosulfates in the laboratory experiments and on filters from Pasadena, USA and Lahore, Pakistan, concluding that OSs from the oxidation of anthropogenic precursors may contribute to urban SOA. The results are novel and would be of interest to the readers of ACP; however, I would not recommend this manuscript for publication because it is not well-written and the conclusions are highly speculative. In particular, the proposed chemical mechanisms from the laboratory experiments are not substantiated by a fundamental knowledge of the chemistry occurring in the reaction chambers used. The authors inconsistently address the fate of the RO2 radical within their laboratory experiments throughout the text and within the proposed mechanisms. There seems to be a mix of RO2 reacting with RO2, HO2, and NO, though they claim different regimes depending on what mechanism they are proposing to explain the OSs formed. For example, they state that reaction with NO is insignificant, yet they report a nitrate containing OS in the decalin system.

First, with regard to RO_2 chemistry: as demonstrated by Ehn et al. (2014), at ppb levels of NO (1-5 ppb; NO concentration in our study, < 1 ppb based on NO measurement) competition exists between RO_2 + NO, RO_2 + HO_2 and RO_2 autoxidation reactions. Nevertheless, ELVOC, though reduced, still formed, indicating that auto-oxidation does not occur solely under pristine conditions. It is important to point out that the high concentrations of VOCs used in this work favor involvement of RO_2 + RO_2 chemistry. In addition, previous work (Crounse et al., 2013), has also reported different RO_2 regimes, such as autooxidation or RO_2 + HO_2 reactions, in experiments using methyl nitrite as an OH radical source, similar to isopropyl nitrite used in our study. As discussed below in response to reviewer's comment # 10, RO_2 + NO reactions are minimal; however, the nitrated OSs at *m/z* 326 are also measured in low concentrations (ng/m^3, Table S3).

Second: we do not claim that the proposed mechanisms represent the major reaction pathways of the photooxidation of the studied alkanes, but are tentatively proposed to explain the formation of the OSs identified in this study. Mechanisms have been clearly indicated as *proposed* branching of pathways of the alkane photooxidations presented to explain formation of specific OSs products consistent with MS^2 data. This approach to rationalizing OH oxidation products is universally applied in oxidation studies (Yee et al 2013; Bugler et al., 2015). Furthermore, the concentrations reported in Tables S1-S3 emphasize the fact that identified compounds are in low abundance regardless of the mass of SOA measured in all experiments.

Finally: we stress to Reviewer #3 that neither the analytical work nor the interpretation of the MS^2 data were questioned. The tandem MS data are consistent with the structures proposed for products observed in both the lab-generated and ambient aerosol samples and we repeat that we clearly indicated in the text that the mechanisms presented are suggested as pathways leading to ions consistent with those observed and until authentic standards become available both the product structures and mechanisms of formation remain tentative. An additional and crucial comment we make is that the major objective of our study is to demonstrate that aliphatic organosulfates form via alkane oxidation, and offer one explanation for reports of aliphatic OSs in urban areas (Ma et al., 2014; Tao et al., 2014).

They propose the formation of hydroperoxides in the case of dodecane experiments with high initial precursor concentrations and do not propose RO2 + RO2 chemistry, but for the C10 systems RO2 + RO2 reactions are proposed with some RO2 + HO2 reactions. They propose epoxide precursors in the C10 systems to OS formation, but not in the C12 system. In general, the proposed mechanisms are arbitrary and do not demonstrate careful control in the design of the experiments or understanding of the chemistry. This lack of understanding becomes clear because there are several areas where citations are used to support the current work, but the citations are used imprecisely and out of context. The manuscript would benefit from more clearly stated organizational structure (e.g. why some mechanisms are proposed in the main text versus the supplemental information).

First we would like to point out that pathways have been proposed that lead to structures consistent with the mass spectrometric data acquired for the observed OSs. We have not attempted to hypothesize general mechanism that would be predicted to give the entire array of precursors contributing to the total mass of SOA. Regarding the possibility of an epoxide precursor to OS-279, we considered the possibility of formation of OS-279 from the reactive uptake of the corresponding epoxide ($C_{12}H_{24}O$); however, the composition of OS-279 (1 DBE) is inconsistent with reactive uptake of an epoxide. Therefore, we have used the few studies available in the literature (Yee et al., 2012; 2013) to propose the formation of OS-279 from the heterogeneous chemistry of hydroperoxides. Finally, we have considered the potential heterogeneous chemistry of hydroperoxides formed from the photooxidation of decalin and cyclodecane as discussed above.

The authors should also clarify motivation in the experimental selection of two C10 cyclic alkane structures and one C12 straight chain structure.

These compounds have been selected due to their potential contribution to SOA formation in the atmosphere. Recent studies have investigated the SOA formation from decalin and dodecane oxidations and reported large SOA yields (Yee et al., 2013; Hunter et al., 2014). Moreover, Pye and Pauliot (2012) have shown that, even though less emitted into the atmosphere, the cyclic C_{10} alkanes have a greater potential for SOA formation than linear or branched alkanes $< C_{12}$.

A few sentences have been added to better explain our selection of parent VOCs on lines 118-122:

"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 (Lim and Ziemann, 2005; Pye and Pauliot, 2012). Alkanes $\geq C_{10}$ are considered as effective SOA precursors, especially when placed in the context of their emission rates (Pye and Pauliot, 2012)."

The brevity of the discussion of results on the OSs from dodecane photooxidation are quite brief relative to the other sections interpreting the results from decalin and cylodecane, and the effects of chemical structure are glossed over in brevity.

As mentioned in lines 229-231, low abundances of OS-209 and OS-237 precluded acquisition of high-resolution MS^2 data, and thus, structures have not been proposed for the parent ions. Without structural information, discussion of formation pathways is not possible. The criticism of our conclusions as "highly speculative," is not consistent with request for more detail on the chemical structure of products formed in abundances too low to obtain high-resolution MS^2 data.

Further, it is unclear if the conclusion that enhancement of OS yields are due to increased acidity of the seed aerosol is really due to acidity, rather than an effect of seeding the experiments with an atomized solution containing more sulfate. These concerns are outlined in detail below.

This point has been previously discussed and published work demonstrates that acidity, rather than concentration of sulfate, is the key parameter (reference cited in the article) in the formation of OSs. Chan et al. (2011) have reported that the formation of OSs from the oxidation of β-caryophyllene is directly correlated with the aerosol acidity ($[H^+]$).

Major Comments:

1. Lines 58-61: These lines are specious in the use of citations and misleading. First, as written, these lines assert that the underestimate of global SOA is equivalent to an underestimate in urban SOA. Second, the references cited (Pye and Pouliot, 2012; Tkacik et al., 2012) do not specifically argue that the underestimate in predicted SOA is due to the omission of IVOCs. A better reference here based on the lines as written would be (Robinson et al., 2007). Pye and Pouliot, 2012 can be cited for exploring additional mechanisms (oligomer formation) from alkane and PAH in SOA formation, and Tkacik et al., 2012 can be cited for providing additional evidence that IVOCs may be a missing source in modeling urban SOA, but the authors need to reword these lines carefully and be more precise.

   Sentence has been modified on lines 59-62 as follows:

   "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)."

2. Line 65: References here should include Yee et al., 2013 which more specifically addresses analogous to Lim and Ziemann, 2005 the products and mechanisms of C12 alkanes of varying structures.

   References have been added.

3. Line 66: Tkacik et al., 2012 should be included here for presenting yields from several alkane systems.

   Reference has been added.

4. Line 71: For this discussion on structure and fragmentation, additional reference should be cited (Lambe et al., 2012).

   Reference has been added.

5. Line 107: The authors assert that acid-catalyzed reactive uptake has not been reported for the oxidation of alkanes. This is not true. Atkinson, Lim, and Ziemann have shown that alkane oxidation leading to 1,4-hydroxy carbonyls convert to cyclic hemiacetals in an acid-catalyzed multi-phase process (Dibble, 2007; Atkinson et al., 2008; Lim and Ziemann, 2009a, 2009b). Schilling Fahnestock et al., 2015 also report the effect of acidity on SOA formation from C12 alkanes.

   This statement has been removed from the revised version of the manuscript.

6. Lines 123-124: Can the authors give more background on these two sites to orient the reader also with the motivation/purpose of this study? What types of sites are these—urban with what type of emissions profiles and surrounded by vegetation, etc.?

   As it is highlighted in the abstract, the motivation for our study was to demonstrate the formation of OSs from the oxidation of alkanes, which has been inferred from previous field studies. Description of both sites is presented in the experimental section and references, which have already characterized both sites, are cited.

   The following sentences have been added:

   Lines 185-188: *"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."*

7. Line 222-223: It would be helpful to label the 1,3-dodecanone sulfate in Figure 1 to aid the reader. The authors should be careful with their naming convention here (i.e. 1,3-), as this particular isomer certainly is not the only potential isomer and is not the only isomer specified in Yee et al., 2012 and Yee et al, 2013.

   The OS has been labeled in Figure 1. We agree with referee #3 that other isomers are present since we identified at least 3 isomers as mentioned on line 236 and reported in Table S1.

   The sentence has been modified on lines 239-242 to*:*

   "Kwok and Atkinson (1995) have reported that OH oxidation of long-chain alkanes 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."

8. Lines 226-230: The reference cited, Ruehl et al., 2013, is improperly used here. Ruehl et al., 2013 describes the heterogenous oxidation of octacosane and finds a strong preference for OH attack at the terminal carbons. The current work, however, is gas-phase oxidation, so the specificity of the isomers as listed in lines 228-229 should be rethought. Further, the naming convention for these isomers are inconsistent with the naming convention in line 222-223. It seems as though the 1, 3-dodecanone denotes the 1 position as the ketone, whereas here the reference to 2, 4-, 3,5-, and 4,6- and other isomers suggests the 1 position is likely the carbon at the end of the dodecane chain.

   Sentence has been removed and naming of the molecule is now consistent with line 242. As discussed by Kwok and Atkinson (1995), reaction occurs preferentially on internal carbons and the sentence has been changed as proposed in the previous point.

9. Lines 234-237: This is a poorly worded sentence. It is unclear in relation to the context of the current work, and there is imprecise use of citations. Hydroperoxides can undergo further oxidation by reaction with OH, but to generate alkoxy radicals from hydroperoxides, that would likely include photolysis. The authors need to address the extent of photolysis in the experiments then. Or are the authors referring to reactions of

RO2 + NO to generate alkoxy radicals? If so, then the authors need to address the extent of RO2 + NO occurring in the experiments. If the former, rewrite as, "First-generation hydroperoxides can undergo further oxidation by reaction with OH to form low-volatility, more highly oxidized products, or can be photolyzed to alkoxy radicals (RO) to form more highly volatile products." The use of Carasquillo et al., 2014 here is inappropriate to discuss the oxidation of hydroperoxides as written. Carasquillo et al., 2014 describe the fate of differing alkoxy radical structures and how it affects SOA yield. The authors need to clarify what they are trying to say here and how it relates to the mechanism proposed in Figure 1.

We thank the reviewer for its comments, sentences have been changed to simplify and clarify this paragraph.

Lines 249-255: "*First-generation hydroperoxides ($C_{12}H_{26}O_2$) can undergo further oxidation by reaction with OH to form either more highly oxidized products, such as dihydroperoxides ($C_{12}H_{26}O_4$), or semi-volatile products ($C_{12}H_{24}O$) (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.*"

10. Lines 237-243: The authors can cite Raff and Finlayson-Pitts, 2010 for IPN as an OH radical source, but it cannot be cited to fully account for the chemical conditions (i.e. the fate of RO_2) in the current experiments without considering the differences between their experiment and that of Raff and Finlayson-Pitts, 2010. The authors should report NOx levels in these experiments to verify the claim that RO2 + NO reactions are minimal. Also, how is O3 formed in these experiments? The authors need to calculate (considering the relatively high levels of initial hydrocarbon), the relative fate of RO2 between reaction with RO_2, HO_2, and NO. The proposal that OS-279 stems from hydroperoxide species in Figure 1 seems least inappropriate if RO_2 fate is really dominated by reaction with RO2 and/or NO.

    In order to provide additional support for the proposed mechanisms, total organic peroxide measurements have been performed. These results which are now reported in Table 1 reveal that organic peroxides (including hydroperoxides) could contribute up to ~ 28 % (on average) of the SOA mass formed from the photooxidation of the precursors used in this work. These measurements highlight the significant presence of organic peroxides and/or hydroperoxides in aerosol and thus support the proposed mechanisms. In addition to the organic peroxide measurements, concentrations of O_3 and NO were also added in Table 1 to confirm the low-NO conditions cited in this work.

The description of the organic peroxide measurements has been added, lines 211-219, revised manuscript:

*"**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 reported values (Docherty et al., 2005; Surratt et al., 2006)."*

A discussion of the results of the organic peroxide measurements has been added, lines 261-265, revised version*:*

"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 RO_2 + RO_2/HO_2 *and/or* RO_2 *autoxidation to SOA formation from alkane oxidations."*

In our experiment we did not add NO (prior to IPN injection) and background NO levels were measured near the detection limit of the NO_x monitor (i.e., 1 ppb). After IPN injection a significant increase of O_3 was observed in all experiments (as described lines 258-260) and NO concentration dropped below 1 ppb. We agree that NO_2 is photolyzed in these systems and NO is recycled. However, under the conditions described here (and in the article on lines 258-260 and in Table 1) most of the NO is expected to react with O_3. Rate constants for the RO_2 + NO and NO + O_3 reactions were determined to be 4.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (k_1) (suggested by MCM; Ehn et al., 2014) and 1.8×10^{-14} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2000; IUPAC) (k_2), respectively. Gratien et al. (2010, ES&T, 44, 8150-8155) have calculated the OH radical concentration to be 5×10^6 molecule cm^{-3} from the photolysis of 5 ppm of isopropyl nitrite (IPN). In our experiments, 0.1-0.25 ppm of IPN was injected into the chambers. Using similar OH radical concentration to Gratien et al. (2010, ES&T) as an upper limit, RO_2 concentration could be estimated to be at ppt levels. Therefore, under the conditions of our study and assuming an O_3 concentration of 0.5 ppm, NO would react predominantly with O_3: $(k_2[O_3]\,[NO])/(k_1[RO_2]\,[NO]) > 350$.

Lines 258-260 have been modified:

"Although RO_2 radicals could also react with NO formed by either IPN or NO_2 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, RO_2 + NO reactions are not expected to be significant."

Finally, the photooxidation of dodecane has been also investigated using an additional injection of NO (200 ppb) prior IPN injection. NO concentration dropped below the ppb level in less than 1 hour and OS concentrations were significantly reduced (factor of 3-4) compared to other experiments, confirming that NO concentration does have an impact on OS formation.

One sentence has been added to describe this experiment, lines 274-277:

"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 OS, such as OS-279."

11. Table 2: The authors never describe the origin of the C7 (OS-209) and C9 (OS-237) organosulfates observed in the dodecane system and also observed in the ambient samples. This is another indication that fragmentation pathways are at play, potentially through RO2 + NO reactions in the system. The authors need to be careful in explaining the fate of the RO2 radical in their experiments and whether the ambient observation of these OSs can really be attributed to dodecane chemistry in the atmosphere when they may clearly originate from other precursors. The authors need to also describe the potential influence of monoterpenes at the sites they have taken samples from to preclude OS origin from biogenic precursors, as they say themselves that C10 monoterpene OSs are isomeric to some proposed in the C10 alkane systems. How good is RT matching/SICs

for confirming that the laboratory generated OSs are really the same as those in ambient data? What measurements in these locations suggest that decalin, cylodecane, and dodecane are prevalent here?

As mentioned in lines 229-231, low abundances of OS-209 and OS-237 precluded acquisition of high-resolution MS^2 data, and thus structures have not been proposed for these parent ions. Without any compositional information, reaction pathways cannot be discussed. As shown by Yee et al. (2012), hydroperoxides can be photolyzed to RO radicals, which fragment to smaller carbonyls. The potential formation of RO radicals from photolysis of hydroperoxides has been added in the revised version of the manuscript.

Isobaric compounds could likely be formed in the atmosphere, however, structures would be significantly different and isomers could be distinguished in most of the cases. Although we cannot completely rule out co-elution of some isobars, Figure 7 illustrates the most likely typical situation, in which isobars from the photooxidation of cyclodecane and decalin have different retention times (R.T.), allowing differentiation. OSs are known to form from the oxidation of monoterpenes and several isobaric OSs have been identified: OS-249, -251, -267, -279 and -326. Structures proposed in previous work are significantly different from structures proposed in this work and thus should be separated by liquid chromatography. We have analyzed ambient filters collected during SOAS campaign in rural areas (Centerville, Alabama, US) and find that the R.T.s of monoterpene-derived OSs are different from those of the OSs identified from the oxidation of the alkanes studied in this work.

For example:

OS-249: from monoterpenes: 10.3 min; cylodecane: 8.5/9.3

OS-279: from monoterpenes: 6.2 min; cylodecane: 5.8/6.8

We do not have access to potential collocated measurements during both field measurements, however, results proposed by Gentner et al (2012) tend to support significant emissions of long-chain alkanes in California and especially during CalNex.

The following sentences have been added:

Lines 185-188:

"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."

11. Lines 246-247: The citation of Claeys et al., 2004 is inappropriate here. The authors propose that "heterogenous chemistry of gas-phase organic peroxide" is a mechanism for OS and tetrol formation, citing Claeys et al., 2004. Yet, Claeys et al., 2004 state, "The mechanism we suggest, reaction with hydrogen peroxide under acidic conditions in the aerosol liquid phase...," which is not consistent with the heterogeneous mechanism proposed in the current work and in Riva et al., 2015b. The difference in humidity should also affect the distribution of hydroperoxide compounds in the gas/particle phase. The authors should address this in the context of mechanistic explanations for their observations.

    We agree with reviewer that Claeys et al. is an inappropriate reference to be used here and we have removed it. We have shown in previous work and in another manuscript currently under review that organic peroxides could lead to OSs and polyols from aerosol-phase acid-catalyzed reactions. It is not clear how the RH could directly impact the distribution of the hydroperoxides as suggested by the reviewer. However, we have reported that the liquid water content of the aerosol plays an important role, but the acidity has a stronger impact on OS formations.

12. Lines 256: Several citations should be added here. Include reference to works by Lim and Ziemann, Lambe et al., Yee et al., Loza et al., Tkacik et al.

    References have been added.

13. Lines 284-286: The mechanism described in text corresponds with the pathway in Figure S8, pathway c, not pathway a. Authors should rewrite these lines to describe pathway a. It also becomes clear here that the authors are not consistent with description of the chemistry proceeding in the chamber. In Figure S8, the fate of RO2 is initially reaction with RO2, but then in pathway a, it shifts to RO2+HO2. The selected pathways seem arbitrary to explain the proposed structure in Figure 2a.

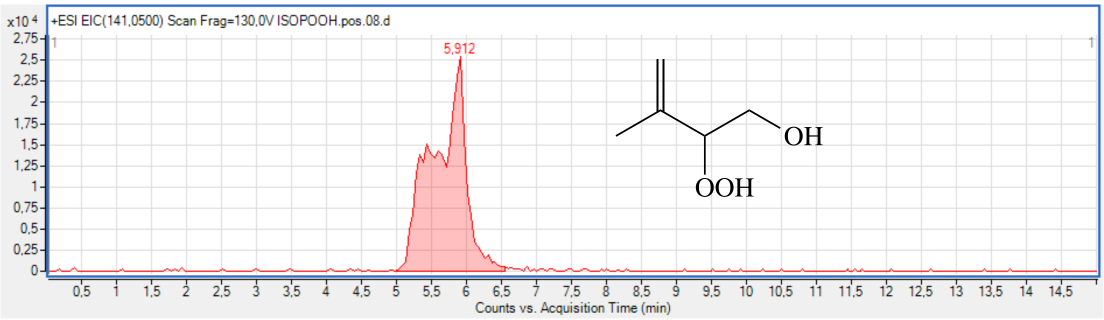
    Figure S8 describes sequential reactions via RO_2 leading to a ring opened ketoperoxy transient. Three branching reactions are available to transient: reaction with HO_2 leading to the structure proposed for OS-265, pathway **a**; further reaction with an RO_2 species leading to the structure proposed for OS-265 and OS-281, pathway **b**; or isomerization and reaction with O_2 eventually leading to OS-281 and OS-297, pathway **c**. Figure S8 does not therefore represent a "shift" in chemistry, but branching reactions leading to three observed product ions. We note that the RO radical precursor to pathways a, b and c may also result from an $RO_2 + HO_2$ reaction (Kautzman et al., 2010; Birdsall et al., 2011). Since it is not possible to distinguish whether RO originates from $RO_2 + RO_2$ or $RO_2 + HO_2$ reactions the alternative $RO_2 + HO_2$ reaction has been added to all mechanisms.

This paragraph has been changed to be consistent with proposed mechanism.

Lines 310-314: *"A scheme leading to the structure proposed in Figure 2a is based on the 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 ($C_{10}H_{18}O_3$) (Yee et al., 2013). $C_{10}H_{18}O_3$ could then further react with OH radicals and lead to an epoxide and sulfate ester by reactive uptake/heterogeneous chemistry (Paulot et al., 2009)."*

14. Line 290: It is unclear whether the analytical technique is sufficient for seeing hydroperoxide moieties on molecules as they are included in the proposed structures. Were hydroperoxide standards such as t-buytylhydroperoxide or cumene hydroperoxide run using this method to verify that the hydroperoxide moiety can be retained on the column? Or is there something about the organosulfates that allow for this? The authors should address this in the experimental methods section as well.

    Such compounds can be retained on the column used in this project and we have demonstrated this for another project with a synthetic isoprene hydroxyhydroperoxide standard (ISOPOOH). As an example, please see the chromatogram below:



Moreover, Witkowski and Gierczak (2012) have recently developed a method to quantify hydroperoxide compounds formed from the ozonolysis of cyclohexene. The authors used a column similar (C_{18}) to that used in the present work. Electrospray ionization mass spectrometry operated in negative mode (Cech and Enke, 2001; Witkowski and Gierczak, 2012) is not highly sensitive to detection of non-acidic compounds, such as pure hydroperoxides or alcohols. However, LC/ESI(-)-MS provides excellent sensitivity for multifunctional compounds (like hydroperoxides and alcohols) containing the OS functional group, since the OS functional group yields an intense $[M - H]^-$ ion, as reported in many studies (Surratt et al., 2008; Kristensen et al., 2011; Kundu et al., 2013; Hansen et al., 2014).

As mentioned line 340-342, we expect to detect the presence of hydroxyl or hydroperoxide functional groups when the OS group is present in the multifunctional compounds analyzed by LC/ESI(-)-MS.

The following sentences has been added:
Lines 340-346: *"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)."*

15. Lines 295-296: The work of Yee et al., 2013 and Schilling Fahnestock et al., 2015 do not test decalin, so they should not be cited here to support proposed formation of a 1-hydroperoxy radical in the decalin system used in the current work. While the mechanisms laid out in Atkinson, 2000 can apply here, as worded it seems as if the authors are proposing the particular alkoxyl reference.

    In Yee et al. 2013 they studied the oxidation of hexylcyclohexane and cyclododecane and they proposed (Figure 1, sidebar, Yee et al. 2013) a ring scission and formation of a terminal carbonyl hydroperoxide as proposed in Figure 3. We do not claim that both studies have investigated the oxidation of decalin but have used the analogous ring scission sequence to explain our products. To avoid confusion regarding the content of the

Yee citation, we have moved the citation in the text to follow the description of ring scission. Sentence has been modified in the revised manuscript.

Lines 348-352: *"Under low-NO_x conditions, abstraction of a proton α to the ring scission of decalin followed by reaction with O_2 leads to the 1-hydroperoxy radical, 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 ($C_{10}H_{18}O_3$) (Yee et al., 2013)."*

17. Line 298/Figure 3: To guide the reader it would be beneficial to update the mechanism in Figure 3 with the same label of tCARBROOH next to intermediate the authors are referring to
We have now added the formula of the different primary products.

18. Lines 298/Figure 3: Do the authors see evidence of an analogous product in the case of decalin, as the OS-279 that was observed in the dodecane case? The proposed mechanism of carbonyl hydroperoxide heterogenous reactive uptake followed by OS formation should also be considered for the decalin tCARBROOH as well and supported by the measurements/compared on the basis of volatility differences due to carbon number/ring structure and the impact of reactive uptake versus partitioning to the particle phase.
We thank the reviewer for its comment. We have revised the pathways proposed for decalin oxidation products OS-265; -267; -269 and -285 and cyclodecane oxidation products OS-249; -251; -265 and -267 to include reactive uptake of the hydroperoxide on wet acidic aerosols.

The appropriate mechanisms have been updated as well as the manuscript:

Lines 314-316: *"OS-265 ($C_{10}H_{17}O_6S^-$) could also arise from the acid-catalyzed perhydrolysis of the hydroperoxide ($C_{10}H_{18}O_4$) generated from the reaction of $C_{10}H_{17}O_4^{\bullet}$ + HO_2 (Figure S8, pathway b)."*

> Lines 319-325: *"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* O_2 *and a 1,5-H shift (Crounse et al., 2011; Orlando and Tyndall, 2012) and lead to a* 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**."*

Lines 357-374: *"*$C_9H_{17}O_4^{\bullet}$ *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 (*$C_9H_{17}O_7S^-$*). The* MS^2 *spectrum of OS-285 (*$C_9H_{17}O_8S^-$*; 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 formation of reaction of the hydroperoxyperoxyl radical intermediate in pathway **b** with* RO_2 *followed by a 1,4-H shift (Rissanen et al., 2015) and addition of* O_2 *to give a hydroxyhydroperoxyperoxyl radical (*$C_9H_{17}O_5^{\bullet}$*).* $C_9H_{17}O_5^{\bullet}$ *could then lead to an epoxide by isomerization (Iinuma et al., 2009; Surratt et al., 2010; Jacobs et al., 2013; Mael et al., 2015) and form OS-285.* $C_9H_{17}O_5^{\bullet}$ *could also react with* HO_2 *and form the corresponding* C_9*-hydroxydihydroperoxide (*$C_9H_{18}O_5$*), which could then undergo heterogeneous reaction and lead to OS-269 (Figure 3, pathway **b**). Finally, a* C_9*-carbonyl hydroperoxide (*$C_9H_{16}O_3$*) could also be formed from the RO +* O_2 *reaction (Figure 3, pathway **c**), which could then further react with OH radicals and lead to a* C_9*-carbonyl dihydroperoxide (*$C_9H_{16}O_5$*). Hence,* $C_9H_{16}O_5$ *could form OS-267 (*$C_9H_{15}O_7S^-$*) from heterogeneous reaction on acidic aerosols."*

19. Lines 299-301: (e.g. remote areas). Please also refer to and reference (Peeters et al., 2009; Crounse et al., 2011; Orlando and Tyndall, 2012). The authors need to justify why the basis of their proposed mechanisms for OS formation rely on this pathway when (e.g. Figures 3, 4, and S8). Is it RO2 + RO2, RO2 + HO2, RO2 + NO, RO2 isomerization?

    The suggested references have been added to the revised manuscript.

As discussed previously, different regime of RO_2 radicals could exist, either terminal (RO_2 + HO_2; RO_2 + RO_2; RO_2 + NO) or autooxidation reactions. In this study, we do not claim to propose all chemical pathways from the oxidation of the alkanes are examined. In most of the mechanisms we have considered the different potential RO_2 reactions (RO_2 + RO_2; RO_2 + HO_2; RO_2 + RO_2, and RO_2 autooxidation), which could lead to the identified OSs through multiphase chemistry of the products shown in the tentatively proposed mechanisms. RO radicals might have formed for other minor chemical channels, such as ROOH + hν or RO_2 + NO, which were not initially included in the manuscript. It is important to note that these potential reactions, which are now included in the manuscript, do not change the different mechanisms tentatively proposed in this study. In addition we have proposed reaction sequences based on known/reported reactions that will lead to products consistent with the mass spectrometric data. This is the same approach used by other investigators, such as Yee et al. (2013).

20. Lines 301-305: The authors should address the extent of photolysis reactions affecting the fate of the proposed hydroperoxides and aldehydes in the system.

    Potential photolysis reactions are now discussed in the revised manuscript. We have incorporated the potential photolysis of hydroperoxides leading to RO radicals and also the photolysis of the aldehyde proposed in Figure 3, which could lead to the RO_2 radical ($C_{10}H_{17}O_5^{\bullet}$).

    Lines 353-357: *"The aldehydic intermediate in the sequence following C_1-C_2 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 O_2, reaction with RO_2 or HO_2 and decarboxylation of the resulting acyl-oxy radical (R(O)O) (Chacon-Madrid et al., 2013) to a hydroperoxyperoxy radical ($C_9H_{17}O_4^{\bullet}$)."*

21. Line 306: "previously unreported" is unclear. Do the authors mean previously unreported in ambient data or previously unreported from similar experiments?

    OS-267 has been identified in previous smog chamber experiments. Sentence has been modified in the revised manuscript.

    Lines 370-374: *"Finally, a C_9-carbonyl hydroperoxide ($C_9H_{16}O_3$) could also be formed from the RO + O_2 reaction (Figure 3, pathway **c**), which could then further react with OH* *radicals and lead to a C_9-carbonyl dihydroperoxide ($C_9H_{16}O_5$). Hence, $C_9H_{16}O_5$ could form OS-267 ($C_9H_{15}O_7S^-$) from heterogeneous reaction on acidic aerosols."*

22. Line 311: As worded, OS-267, is proposed to originate from further oxidation of OS-269, but the arrows drawn in Figure 3 are inconsistent suggesting origin from the epoxide.

    We have corrected the revised manuscript.

23. Line 327/Figure 4: The description of Ring cleavage of the C10 alkoxy radical is not consistent with the "ISO"/isomerization descriptor in Figure 4. Please clarify that pathway.

    ISO descriptor in Figure 4 (*pathway a*) indicates the isomerization of the RO_2 formed from the ring cleavage and lead to hydroperoxide functional group.

    Sentences have been added to better discuss this pathway:

    Lines 382-388: *"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 ($C_{10}H_{15}O_8S^-$)."*

24. Line 340: Figure 1d does not exist. Clarify the reference.

    The reference was Figure 2d and not 1d, the text has been appropriately modified.

25. Lines 343-345: Sentence is awkward beginning with "Pathway c", and from what figure? Clarify that it is Figure 4. Again, citation of Atkinson, 2000 seems inappropriate as the sentence is written.

    Sentence has been changed, pathway **c** referred to Figure 4. Citation of Atkinson (2000) was used to support formation of an organonitrate from RO_2 + NO reaction, since it is a common reaction as discussed in the Atkinson's review.

Lines 402-408: *"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 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 ($C_{10}H_{17}NO_3$) with subsequent reactions shown in Figure 4, pathway **c**"*

26. Lines 343-345/Figure 4, pathway c: Here the authors propose that RO2 + NO chemistry is occurring to form a nitrate containing OS. This contradicts the authors' earlier statement in lines 237-243 stating that the RO2 + NO reactions are not significant in their experimental setup. The authors need to handle in more detail the fate of RO2 under the unclear experimental conditions.

As demonstrated and discussed by Ehn et al. (2014) at ppb levels of NO (which is even higher than the conditions of our study) a competition exists between RO_2 + NO; RO_2 + HO_2 and RO_2 autoxidation reactions. The Ehn et al. (2014) study demonstrates that ELVOC, even though reduced, are still formed at NO concentrations greater than few ppb. It is important to point out that the concentrations of VOCs used in this work could also lead to RO_2 + RO_2 chemistry. Therefore, not only one RO_2 reaction could occur and the different RO_2 reactions have to be considered, which has been done in this study.

O_3 and NO concentrations are provided in the revised manuscript (Table 1). In addition a paragraph has been added describing the fate of RO_2.

Lines 404-406: "*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.*"

27. Lines 349-364: Why is discussion of OS-281 and OS-297 featured here, when discussion of OS- 265 is discussed near the beginning of Section 3.2? Since they are all referenced in Figure S8, their chemistry should be discussed together from the same mechanistic precursors.

We chose to describe the formation and tentative structural assignments of ions observed on ambient filters at the beginning of the discussion, as explained in the manuscript on lines 293 to 295 ("*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. The selected OSs were, as described in the next section, quantified and characterized in the fine urban aerosol samples.*").

However, section 3.2 has been reorganized as requested by the reviewer #3 and formation pathways of OS-265, -281 and -297 are included in the same paragraph.

28. Section 3.2: Authors should clarify the main mechanistic differences and relative importance between Figure S8, Figure 3, and Figure 4, and the flow of products to be discussed at the beginning of Section 3.2. Currently as written, the flow of Section 3.2 is very arbitrary when choosing different OS products to discuss.
    We decided to separate the different reaction pathways for clarity since it would not have been clear and quite difficult/confusing to propose in one figure the formation pathways of all OSs. The different reaction pathways are separated based on OSs that are generated from branching reactions of a common transient. This section has been modified as discussed in the previous point. The importance of the proposed pathways cannot be evaluated based on this study and this was not the study objective.

    We have added a sentence to clarify this point.
    Lines 297-299: "*The different reaction pathways presented below, are separated based on OSs that are generated from branching reactions of a common transient*."

29. Lines 377-380: Incorrect use of citations here. Yee et al., 2012 do not propose RO2 + RO2 chemistry and therefore a "precedent" has not been established. The authors should not be citing Atkinson, 2000; Yee et al., 2012 and Raff and Finlayson-Pitts, 2010 to speak for the experimental conditions in the current work. The mechanism of RO2 + RO2→RO can be supported by work on general atmospheric chemistry mechanisms including Atkinson, 2000 and many other works, and so if this mechanistic pathway is to be cited, than many other works should be cited as well.
    We agree with reviewer that Yee et al. is an inappropriate reference and have removed it. General references on atmospheric chemistry have been added: Atkinson and Arey (2003,

Chem Rev, 103, 4605-4638) and Ziemann and Atkinson (2012, Chem Soc. Rev., 41, 6582-6605).

30. Line 379: Inconsistent citation here compared to line 300 for similar mechanistic argument.

    We have cited Ehn et al., 2014 and Jokinen et al., 2014 and Mentel et al., 2015 for both transformations.

31. Figure S14: Why do the authors propose in the case of cyclodecane formation of the hydroperoxide from RO2 + HO2 pathways and subsequent chemistry thereof, but not in the case of decalin in any of Figures 3, 4, and S8? Further, Figure S14 outlines a mechanism from further reaction of the hydroperoxide to get to an epoxide that then enters the particle phase to produce OS-251 and OS-249. This seems like a plausible analogous mechanism to propose for the case of dodecane rather than reactive uptake of a carbonyl hydroperoxide. Why do the authors propose different mechanisms between dodecane and cyclodecane to generate the similar analogs (OS-279, OS-249)?

    As mentioned in the point #18 above, cyclodecane-derived OSs might be formed from the heterogeneous chemistry of hydroperoxides. We have added these different pathways in the different Figures as well as in the manuscript. Please note that we have now combined Figures S14 and S15 to present the OS formation from cyclodecane in one Figure.

    Lines 428-435: *"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)."*

    As described above we proposed different fates for the RO_2 radicals: RO_2 + RO_2, RO_2 + HO_2 and RO_2 autoxidation reactions in the different schemes proposed for the photooxidation of decalin and cyclodecane. RO_2 + HO_2 reactions are also proposed in the case of the photooxidation of decalin, which likely explain the formations of hydroperoxides as discussed above.

32. Section 3.4: This section is weak and little effort is made to really describe the chemical differences between the systems to interpret the findings. There should be comparisons of vapor pressures of the precursors and carbon numbers and discussion of previously published yields from these compounds to support the discussion. How does quantification using the available OS surrogate standards potentially affect the OS quantification across these systems/factoring in different sensitivities?

    The objective of this study is to establish that OSs may be products of the photooxidation of anthropogenic precursors, such as the alkanes examined here, and thus to demonstrate the relevance of this chemistry observations of aliphatic OSs in urban areas (Mao et al., 2014; Tao et al., 2014). Since the reaction pathways leading to the products observed in this study and in ambient samples are tentative, we feel that discussion at the level of thermodynamics is not justified and have deleted Section 3.4.

33. Line 400: The authors claim that "the presence of acidic aerosols significantly increase OS formation in most cases". However, is this just an effect of using an atomized solution with more sulfate (0.06M ammonium sulfate + 0.06M sulfuric acid) in the acidic case versus only 0.06M ammonium sulfate in the non-acidified case? It may be a concerted effect of more available sulfate in the "acidic" case as well as acidity.

    It has been demonstrated in previous studies (cited references) that acidity rather than the concentration of sulfate is a key parameter in the formation of OS. Chan et al. (2011) demonstrate that the formation of OSs from the oxidation of β-caryophyllene is directly correlated with the aerosol acidity ($[H^+]$).

34. Line 484: The authors return to claim that the experiments are conducted under dominant "RO2/HO2" chemistry—this is contradictory to the formation of OS-326 containing a nitrate group.

    This issue has been discussed previously in response to reviewer comments # 10, 13, 19, 26, and 31 above.

35. Lines 484-486: Enhancement of OS due to acidified ammonium sulfate seed needs to be addressed with regard to the effect of just having introduced more sulfate into the experiments compared to the non-acidified case. See earlier Major Comment, 33.

    As discussed in response to Reviewer comment # 33, enhancement of OSs has been demonstrated to result from an increase of the aerosol acidity (cited references) and our work is consistent with these studies.

36. Lines 491-496: The "novel pathway" involving reactive uptake of hydroperoxides is not well- substantiated in the current work and is mostly speculation. The vapor pressure alone of the carbonyl hydroperoxide makes it a potential candidate to partition to the particle phase, not via reactive uptake. There are no direct measurements of hydroperoxides in the gas phase, and insufficient discussion on if hydroperoxides are detected in the particle phase using the UPLC technique. Further, if reactive uptake is at play, why have the authors not seen the corresponding decalin analog of carbonyl hydroperoxide?

    We agree with reviewer #3 that "reactive uptake" of hydroperoxides is currently not well substantiated, and have clearly indicated that this pathway is tentative. With regard to reactive uptake and perhydrolysis of carbonyl hydroperoxides generally as an alternative pathway the revised manuscript cites this route as a possibility in the formation of 8 OSs, as indicated in response to earlier comments. Also as discussed above in response to Reviewer comment #14, LC-EI/MS in the negative ion mode, used to identify the OS products, will not detect analytes (such as hydroperoxides) not containing substituents readily yielding negative ions.

Minor Comments:

1. Line 30: "Both studies strongly support formation of OSs" is awkward. Reword, for example, "Both studies strongly support that OSs can form from the gas-phase oxidation of anthropogenic precursors..."

   The wording has been revised on lines 30-33 as follows:

"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."

2. Line 48: Change "aerosol" to "particles", as aerosol is technically defined as both gas + particle.

   The wording has been revised as suggested.

3. Line 76: Insert comma after "2015)".

   A comma has been inserted.

4. Line 83: Change comma to semi-colon after "2007,".

   A semi-colon has been inserted.

5. Line 90: Delete "of".

   Use of "of" is appropriate and we have not made this change.

6. Line 103: Change "reduce" to "reduces".

   The revision has been made as suggested.

7. Line 136: Check misprint on the high humidity range listed as "(4-60%)".

   The correction has been made (i.e. 40-60%).

8. Line 220: Insert after ")", ", hereafter referred to as OS-279, ".

   The change has been made as suggested.

9. Line 268: "ion at m/z 265.0749" should be "ion at m/z 265.0752" according to Figure 2.

   "at" has been inserted.

10. Line 315: Add in "Figure 3, pathway a" to be clear.

    "Figure 3, pathway a" has been inserted.

11. Line 345: Change "identical" to "analogous" as the sequence of reactions are certainly not identical as shown in Figure 4.

    "Analogous" has been substituted.

12. Line 350: Change chemical formula to include S for OS-281.

    The formula has been corrected.

13. Line 352: Rewrite the sentence. The radical reacts with O2, followed by 1,6 H shift, etc.

    Sentence has been modified on lines 319-325 to:

    *"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 O_2 and a 1,5-H shift (Crounse et al., 2011; Orlando and Tyndall, 2012) and lead to a 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**."*

14. Lines 362-363: Rewrite the awkward phrasing, "which be reactively taken up to give a sulfate ester".

    Sentence has been changed.

    Lines 331-334: *"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."*

15. Lines 371-374: Poor grammar. Rewrite sentence.

    The sentence has been changed on lines 419-422 to:

    "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."

16. Line 379: "hydroperoxydes" is spelled wrong.

    The spelling has been corrected.

17. Line 459: Add “of” after “oxidation”.

    “of” has been added.

18. Line 482: Add “,” after “cyclododecane”.

    The comma has been added.

Additional References:

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Chemical Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of Alkanes

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The authors declare no conflict of interest.

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.

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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).

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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

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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 of 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

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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.

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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 (Iinuma 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 (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).

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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

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(Lim and Ziemann, 2005; Pye and Pauliot, 2012). Alkanes ≥ C_{10} 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, $PM_{2.5}$ samples collected from Lahore, Pakistan and Pasadena, CA, USA were analyzed to detect and quantify OSs identified from the smog chamber experiments.

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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 (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 $(NH_4)_2SO_4$ or 0.06 M $(NH_4)_2SO_4$ + 0.06 M H_2SO_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 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 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

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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.

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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 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.

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 ($SO_3^{\bullet/-}$), 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 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 ($C_{12}H_{23}O_5S^-$, 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

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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 ($C_{12}H_{26}O_2$) can undergo further oxidation by reaction with OH to form either more highly oxidized products, such as dihydroperoxides ($C_{12}H_{26}O_4$), or semi-volatile products ($C_{12}H_{24}O$) (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, 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 could also react with NO formed by either IPN or NO_2 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, RO_2 + 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 RO_2 + RO_2/HO_2 and/or RO_2 autoxidation to SOA formation from alkane oxidations.

Carbonyl hydroperoxide ($C_{12}H_{24}O_3$), 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

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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.

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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 $\mu g\ m^{-3}$) 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). 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* 265.0752 (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

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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 $C_{10}H_{17}O_6S^-$ 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 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 ($C_{10}H_{18}O_3$) (Yee et al., 2013). $C_{10}H_{18}O_3$ 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 ($C_{10}H_{17}O_6S^-$) could also arise from the acid-catalyzed perhydrolysis of the hydroperoxide ($C_{10}H_{18}O_4$) generated from the reaction of $C_{10}H_{17}O_4^{\bullet}$ + HO_2 (Figure S8, pathway b). The MS^2 spectrum for the single parent ion at *m/z* 281 corresponding to the composition $C_{10}H_{17}O_7S^-$ (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 a 4-(cyclohexan-2-one)but-1-yl radical followed by reaction with O_2 and a 1,5-H shift (Crounse et al., 2011; Orlando and Tyndall, 2012) and lead to a C_{10}-carbonyl-

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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 $C_{10}H_{17}O_8S^-$ 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 (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 ($C_9H_{17}O_7S^-$) 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 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).

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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 scission of decalin followed by reaction with O_2 leads to the 1-hydroperoxy radical, 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 ($C_{10}H_{18}O_3$) (Yee et al., 2013). The aldehydic intermediate in the sequence following C_1-C_2 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 O_2, reaction with RO_2 or HO_2 and decarboxylation of the resulting acyl-oxy radical (R(O)O) (Chacon-Madrid et al., 2013) to a hydroperoxyperoxy radical ($C_9H_{17}O_4^{\bullet}$). $C_9H_{17}O_4^{\bullet}$ 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 ($C_9H_{17}O_7S^-$). The MS^2 spectrum of OS-285 ($C_9H_{17}O_8S^-$; 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 formation of reaction of the hydroperoxyperoxyl radical intermediate in pathway **b** with RO_2 followed by a 1,4-H shift (Rissanen et al., 2015) and addition of O_2 to give a hydroxyhydroperoxyperoxyl radical ($C_9H_{17}O_5^{\bullet}$). $C_9H_{17}O_5^{\bullet}$ could then lead to an epoxide by isomerization (Iinuma et al., 2009; Surratt et al., 2010; Jacobs et al., 2013; Mael et al., 2015) and form OS-285. $C_9H_{17}O_5^{\bullet}$ could also react with HO_2 and form the corresponding C_9-hydroxydihydroperoxide ($C_9H_{18}O_5$), which could then undergo heterogeneous reaction and lead to OS-269 (Figure 3, pathway **b**). Finally, a C_9-carbonyl hydroperoxide ($C_9H_{16}O_3$) could also be formed from the RO + O_2 reaction

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(Figure 3, pathway **c**), which could then further react with OH radicals and lead to a C_9-carbonyl dihydroperoxide ($C_9H_{16}O_5$). Hence, $C_9H_{16}O_5$ could form OS-267 ($C_9H_{15}O_7S^-$) 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 ($C_{10}H_{15}O_8S^-$) 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 ($C_{10}H_{15}O_8S^-$).

Two isobaric parent ions with identical MS^2 spectra were observed at *m/z* 311 ($C_{10}H_{15}O_9S^-$; 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

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form the sulfate ester on reactive uptake. Abstraction of H1 rather than H6 would lead to an isobaric structure.

Four isobaric ions corresponding to $C_{10}H_{16}NO_9S^-$ 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 ($C_{10}H_{17}NO_3$) 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 $C_{10}H_{16}NO_9S^-$ isobars have also been identified in SOA produced from the gas-phase oxidation of monoterpenes (Surratt et al., 2008).

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

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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 (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

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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.

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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-

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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}.

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

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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, 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 ($C_7H_{15}O_4S^-$), 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; 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

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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 nuclophilic 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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The authors thank the Camille and Henry Dreyfus Postdoctoral Fellowship Program in Environmental Chemistry for their financial support. The authors wish also to thank CAPES Foundation, Ministry of Education of Brazil (award no. 99999.000542/2015-06) for their financial support. This study was supported in part by the National Oceanic and Atmospheric Administration (NOAA) Climate Program Office's AC4 program, award no. NA13OAR4310064. The authors wish to thank Kasper Kristensen and Marianne Glasius (Department of Chemistry, Aarhus University, Denmark) who synthesized the 3-pinanol-2-hydrogen sulfate. The authors also thank Tauseef Quraishi, Abid Mahmood, and James Shauer for providing filters collected in Lahore, in addition to the Government of Pakistan, the Pakistani Higher Education Commission, and the United States Agency for International Development (US-AID) for funding field sample collection in Pakistan.

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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)	[NO] (ppb)	$[O_3]$ (ppb)	T (K)	RH (%)	Final OA mass ($\mu g\ m^{-3}$)	Total Peroxides ($\mu g\ m^{-3}$)
Dodecane	412	N	Non-Acidified	215	< 1	512	304-311	49-59	58	*N.d.*
	420	S	Acidified	212	< 1	528	305-311	51-63	65	*N.d.*
Dodecane	422	N	Non-Acidified	215	< 1	507	302-308	15-20	49	*N.d.*
	427	S	Acidified	212	< 1	538	303-308	14-17	53	*N.d.*
Dodecane	397	N	Acidified	215	< 1	506	304-309	45-52	52	15.4
	409	S	Acidified	212	< 1	585	305-310	15-19	59	15.2
Decalin	175	N	Non-Acidified	138	< 1	327	302-309	48-45	204	*N.d.*
	180	S	Acidified	136	< 1	335	302-308	51-49	224	*N.d.*
Decalin	199	N	Non-Acidified	138	< 1	317	305-306	13-13	200	59.7
	204	S	Acidified	136	< 1	328	306-306	13-14	211	75.5
Decalin	N.I.	N	Acidified	138	< 1	319	302-306	43-54	245	43.9
	N.I.	S	Acidified	136	< 1	324	301-306	9-12	270	57.8
Cyclodecane	257	N	Non-Acidified	172	< 1	374	298-301	53-61	218	76.6
	263	S	Acidified	170	< 1	364	299-301	52-60	238	72.2

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Cyclodecane	256	N	Non-Acidified	172	< 1	350	300-303	13-15	177	57.8
	261	S	Acidified	170	< 1	332	300-302	13-14	210	68.3
Cyclodecane	245	N	Acidified	172	< 1	345	298-300	10-11	259	78.8
	250	S	Acidified	170	< 1	355	299-300	51-49	270	69.2

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

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Hydrocarbons (HCs) ... [25]

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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

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[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.*
$C_9H_{17}O_8S^-$	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

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(285.0651)[a,c]														
$C_{10}H_{15}O_8S$- (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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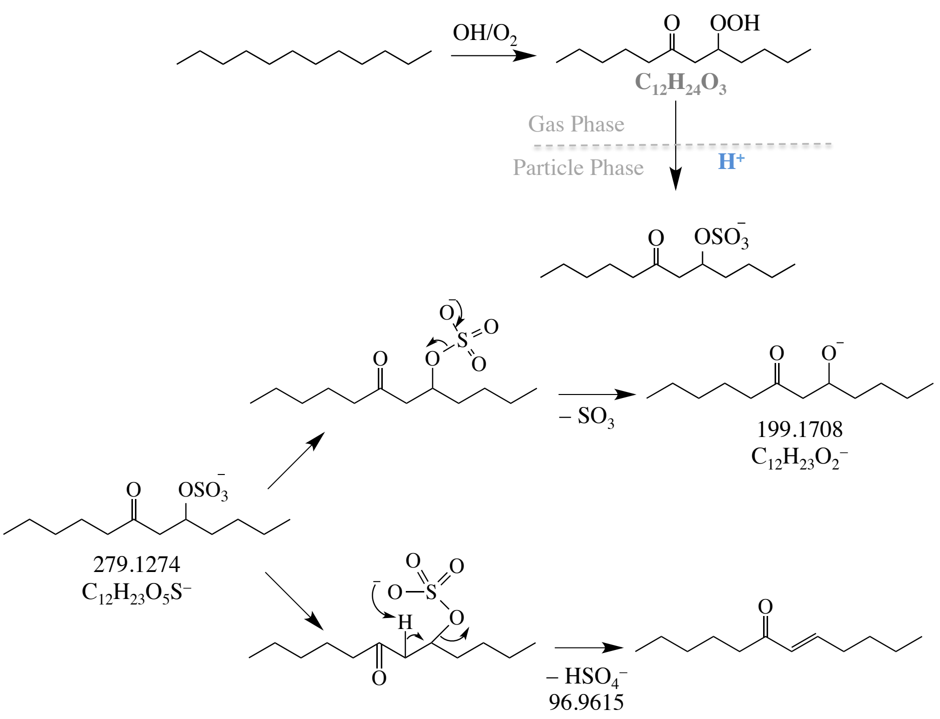

Figure 1. Proposed formation pathway of OS-279 (*m/z* 279.1274) and its corresponding fragmentation routes. The suggested mechanism is based on identified products from previous study (Yee et al., 2012).

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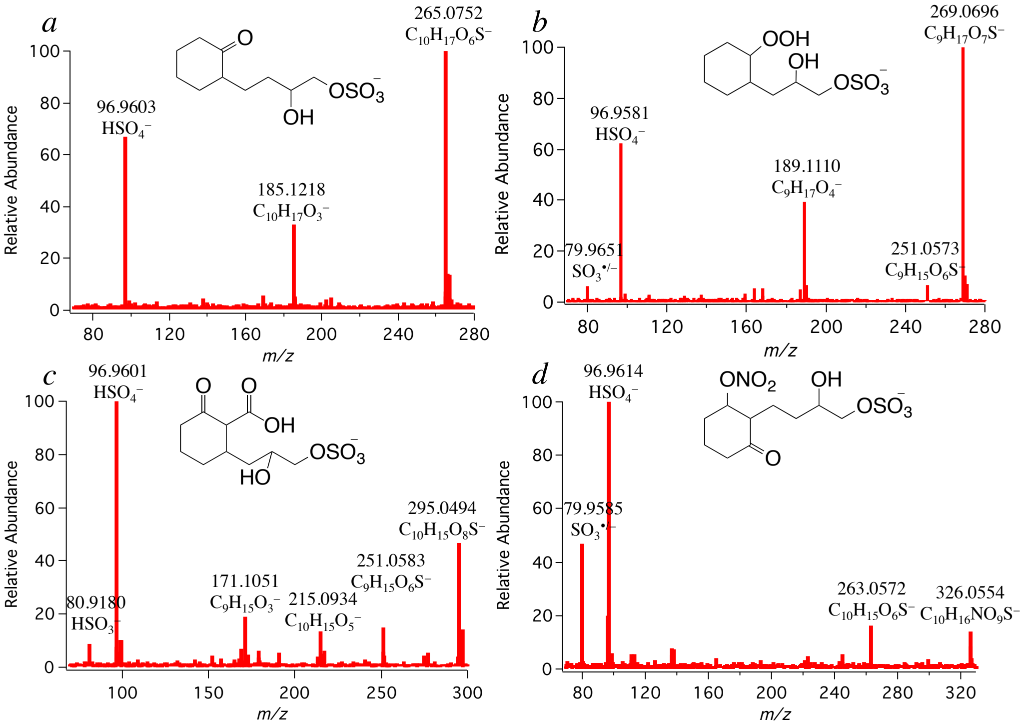

Figure 2. MS^2 spectra obtained for selected decalin-derived OSs: (*a*) *m/z* 265.0752 ($C_{10}H_{17}O_6S^-$), (*b*) *m/z* 269.0696 ($C_9H_{17}O_7S^-$), (*c*) *m/z* 295.0494 ($C_{10}H_{15}O_8S^-$) and (*d*) *m/z* 326.0554 ($C_{10}H_{16}NO_9S^-$). Fragmentation schemes are proposed in Figure S2.

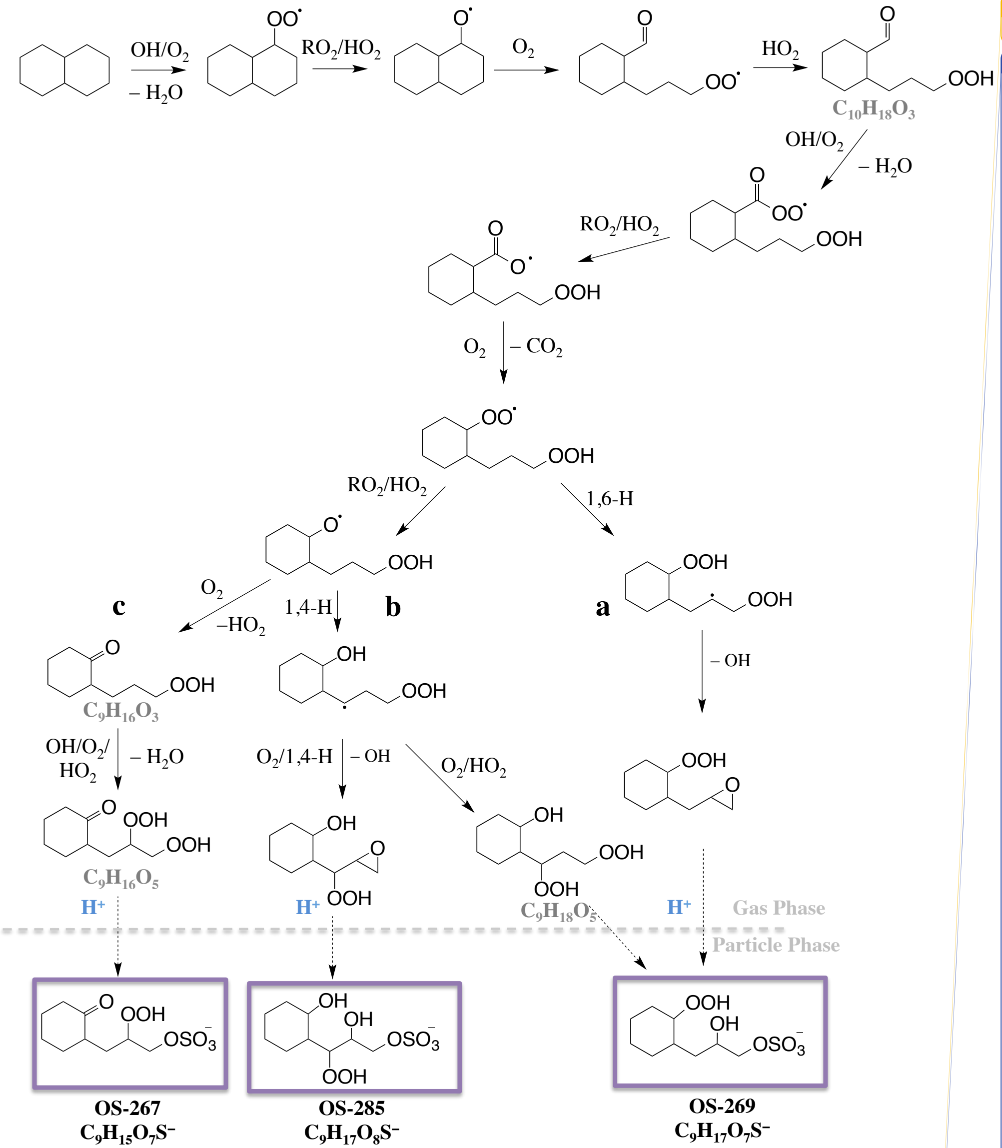

Figure 3. Tentatively proposed formation pathways of OS-267 (*m/z* 267.9552), OS-269 (*m/z* 269.0696) and OS-285 (285.0654) from the oxidation of decalin in presence of sulfate aerosol.

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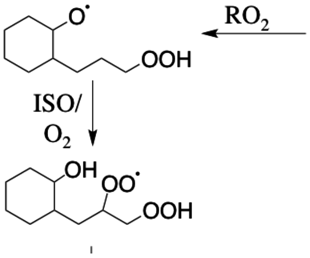

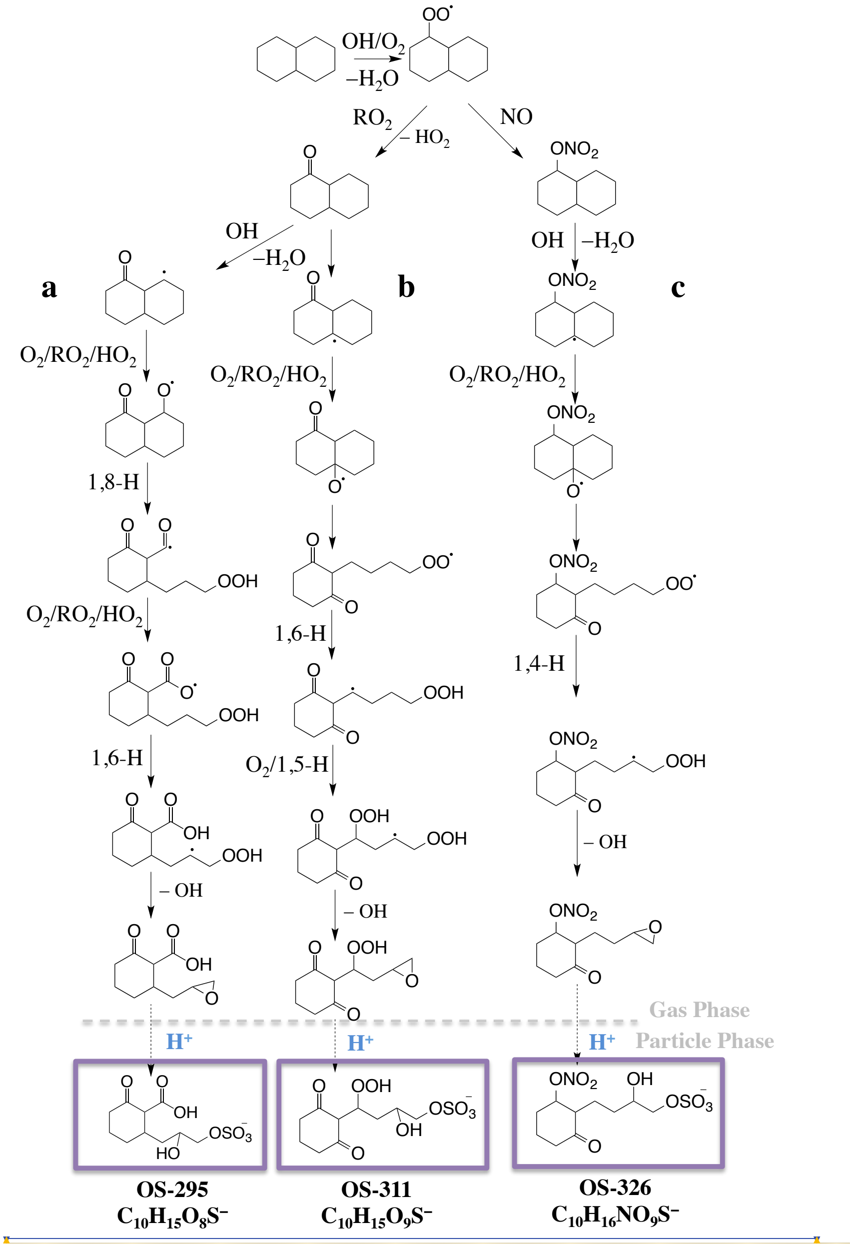

Figure 4. Tentatively proposed formation pathways of OS-295 (295.0494), OS-311 (*m/z* 311.0447) and OS-326 (326.0554) from the oxidation of decalin in the presence of sulfate aerosol.

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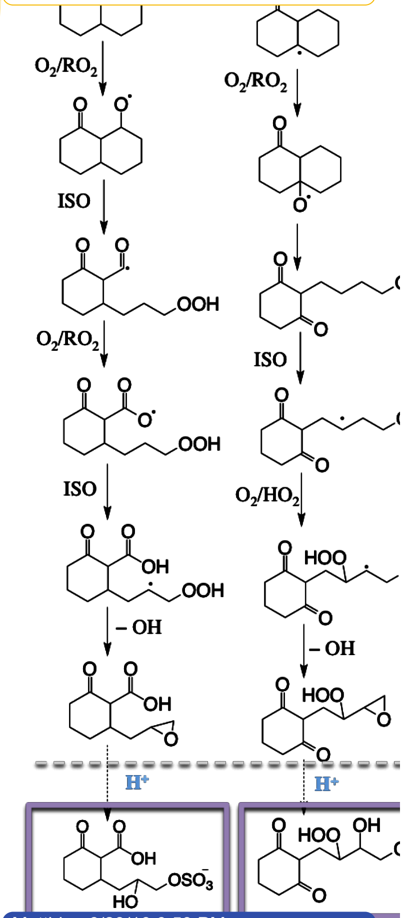

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Deleted: **Figure 4.** Proposed formation pathways of OS-295, OS-311 and OS-326 from the oxidation of decalin in the presence of sulfate aerosol. ISO = isomerization reaction either through H shift (1,5- or 1,7-) or through hyderoperoxide isomerization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

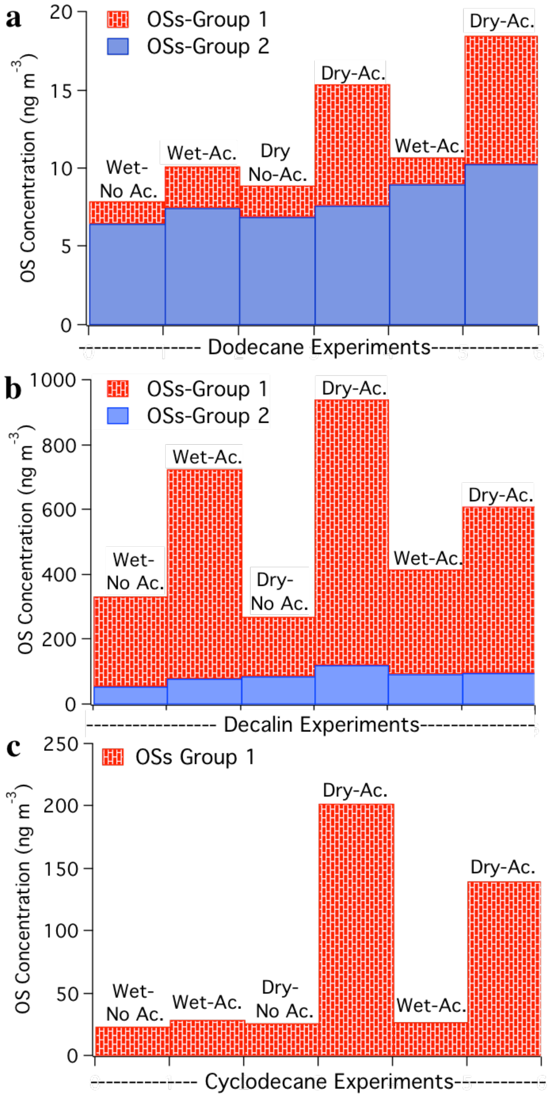

Figure 5. Impact of acidity on OS formation from gas-phase oxidation of (a) dodecane, (b) decalin, and (c) cyclodecane. OSs from Group-1 corresponds to compounds strongly impacted by aerosol acidity, while OSs from Group-2 appeared to have less dependency on aerosol acidity.

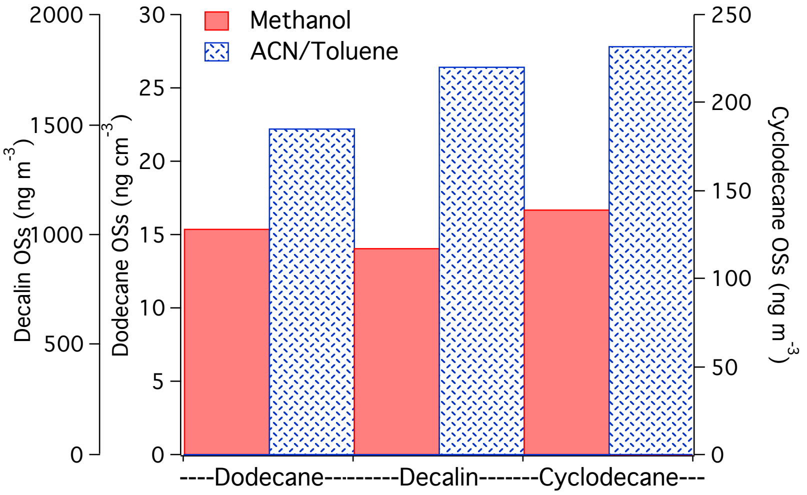

Figure 6. Impact of extraction solvent composition on quantification of identified OSs from gas-phase oxidation of alkanes.

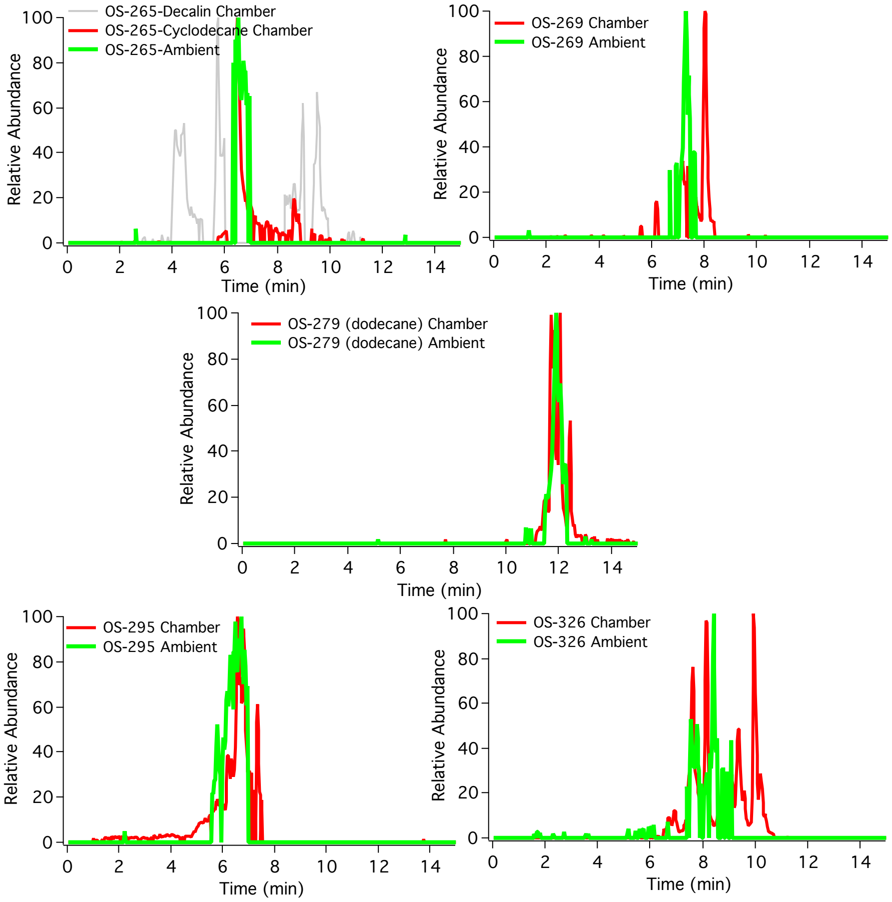

Figure 7. Extracted ion chromatograms (EICs) for selected alkane OSs identified in both smog chamber experiments (in red) and ambient samples (in green).