

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 C₁₀ alkanes have a greater potential for SOA formation than linear or branched alkanes < C₁₂.

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 (< C₁₂) 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 ≥ C₁₀ 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 $\text{RO}_2 + \text{RO}_2$ 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- NO_x 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 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 $4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (k_1) (suggested by MCM; Ehn et al., 2014) and $1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (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 $5 \times 10^6 \text{ molecule cm}^{-3}$ 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 RO_2 - RO_2 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, NO₂, O₃, 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 RO₂ + NO, RO₂ + HO₂ and RO₂ 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 RO₂ 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 RO₂ + RO₂ 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 O₃ 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, Crouse et al. (2013) (reference provided by Referee #2) have also shown that RO₂ autoxidation 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 MS² 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 RO₂ 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 RO₂ + NO, RO₂ + HO₂/RO₂ and RO₂ 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 RO₂ + RO₂/HO₂ and/or RO₂ 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 RO₂ isomerization is much too slow to compete with other pathways (RO₂, HO₂, and NO reactions). See Crouse 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 RO₂ 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 RO₂ was 0.005 s⁻¹ with NO and 0.006 s⁻¹ with HO₂*” under the conditions of this study):

- *“Importantly, there is no evidence for the formation of C₅-hydroxy carbonyl nitrate (Scheme 2, HCN) or C₅-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 HO₂ (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 Crouse 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 Crouse et al.

Formation of OS-285 (Pathway B, Figure 3) is not explained by RO₂ isomerization (even though as discussed by Crouse et al., isomerization through a 5-member ring may be important) but from RO (formed from RO₂ + RO₂ 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 RO₂ followed by a 1,4-H shift (Rissanen et al., 2015) and addition of O₂ to give a hydroxyhydroperoxyperoxyl radical (C₉H₁₇O₅[•]). C₉H₁₇O₅[•] 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. C₉H₁₇O₅[•] could also react with HO₂ and form the corresponding C₉-hydroxydihydroperoxide (C₉H₁₈O₅), 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 CO₂ 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 RO₂ to 2-decalinone, formation of a C₁₀ alkoxy radical followed by ring cleavage of the C₉-C₁₀ decalin bond and further RO₂ isomerization (1,8-H shift) leading to a 4-(carboxy cyclohexyl)-1-hydroperoxybut-2-yl radical

via RO₂ chemistry. Although considered as a minor reaction pathway (Crouse et al., 2013), the acyloxy radical could lead to the epoxide from the isomerization of the O₂ 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 (C₁₀H₁₅O₈S⁻)."

Figure 4, Pathway B. The proposed RO₂ isomerization is much too slow to compete with other pathways (RO₂, HO₂, and NO reactions). See Crouse 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 Crouse 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 Crouse et al. (2013) the intramolecular barrier for H-shift to the RO₂ 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 C₁₀H₁₇NO₆, 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 (Crouse 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 nucleophilic

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.