Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-20-RC2, 2016

Atmospheric Chemistry and Physics
Discussions

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.

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.

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

4. Were background VOCs identified/quantified?

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.

6. Line 239-240: Raff and Finlayson-Pitts do not show that RO2-RO2 chemistry dom-

inates in isopropyl nitrite photolysis, only that it contributes to the chemistry. Because NO2 is photolyzed in these systems NO is recycled and so available for reaction with RO2 radicals, even when O3 is present. 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, 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.

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 Crounse et al., J. Phys. Chem. Lett. (2013), 4, 3513-3520.

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.

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.

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.

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.

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.

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.

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.

Technical Comments

None.

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