

Interactive comment on “Chemical composition of isoprene SOA under acidic and non-acidic conditions: Effect of relative humidity” by Klara Nestorowicz et al.

Anonymous Referee #1

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This paper reports the formation of organosulfates and other oxygenated compounds in secondary organic aerosols (SOA) generated in an indoor smog chamber from isoprene oxidation in the presence of seed aerosols. For several OSs, chemical structures are proposed on the basis of high-resolution tandem mass spectra. Isoprene accounts for a large part of VOCs in the global atmosphere, and its photooxidation has been found to contribute to SOA formation. However, relatively few studies have been focused on the oxidation of isoprene under various relative humidities (RH), and there is still uncertainty on its chemical mechanisms and contribution to SOA formation. While this study might provide valuable information for a better understanding of the chemical pathways from the photooxidation of isoprene, the results presented here are not

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sufficiently supported by the analytical method and/or do not present a real novelty. In addition, the authors should have a closer look at the literature since some of their results (e.g. 2-methyltetrols) are not consistent with the existing literature. Therefore, additional information/references and major revisions would have to be provided in order to consider this article for publication.

General comments: Page 2, lines 8-10: Too simplified, as written gas-phase oxidation of isoprene leads directly to the formation of isoprene-derived SOA products such as 2-methyltetrols. Please detail.

Page 3, line 5. Why did the authors use Kleindienst et al. 2007 as a reference to explain the formation of organosulfate?

Page 3, lines 13-22. Other groups have investigated the impact of RH on the SOA formation from isoprene oxidation: e.g. Abbatt's (isoprene + OH at different RH) & Surratt's groups (reactive uptake of IEPOX under different RH, acidity, . . . ; isoprene + O₃ at different RH and seed).

Page 3, lines 23-24. Couvidat et al. did not incorporate heterogeneous chemistry (i.e. reactive uptake) or the impact of acidity in their model. Pye et al. (2013) and Marais et al. (2016) demonstrate that replacing a reversible partitioning approach with reactive uptake to aqueous aerosol improves agreement with observations. Please revise.

Page 4, lines 18-19. “moderately acidic sulfate aerosol” does not have a real scientific meaning. Please determine the aerosol acidity and liquid water content using thermodynamically model.

Page 4, lines 30-31. Please add additional information. What was the sampling time for the filters? How much mass was collected?

Page 5, lines 17-19: how many filters were analyzed? It is important to know if the tracers were identified in 1, 10 or 100 samples. Please provide some statistical information.

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Page 6. Line 3-19: Additional information/explanation are needed in the analytical protocol to validate the results: - Temperature and pressure in the rotavapor? Did the authors evaluate the losses of the most volatile compounds → tetrols/IEPOX/...? - The authors mentioned that internal standards were used. What is the extraction efficiency/recovery? Why did the author realize this step for the GC-MS analysis only? Extraction/recovery efficiencies have to be provided for both methods.

Page 6, line 27. The authors report a SOA yield of 0.32% and conclude: "The values of SOA yields agree with previous smog chamber studies". It is not exact and some studies have reported SOA yields 10 times higher (Carlton et al., 2009 ACP). The authors should discuss and compare their results in more details. In addition, to really compare apple to apple the authors should discuss the impact of NO/VOC ratio, which can greatly impact isoprene SOA formation (Xu et al., 2014).

Page 7, Table 1. The initial concentration of NO is higher than the steady-state concentration of NO_x (= NO + NO₂). Why? What was the NO₂ concentration? The authors should also discuss the different regimes NO/NO₂ (→ impact SOA yields).

Page 8, lines 1-2. Why did the authors look only at the organosulfates? The authors should compare the quantification of the acids from LC/ESI(-)-MS vs GC-MS and polyol LC/ESI(+)-MS vs GC-MS. Indeed, it is now recognized that all thermal analyses (i.e. GC-MS, FIGAERO, SV-TAG) lead to a subsequent fragmentation of the oligomers. Isoprene-derived SOA is assumed to be mainly made out of oligomers especially under acidic conditions. The authors have the information/analytical tools to provide more insights on this topic.

Page 8, lines 3-4. Please add references

Page 8, lines 8-9. Organosulfate at m/z 230 was previously identified from the oxidation of unsaturated aldehydes.

Page 8, Table 2. Please verify the structures/formulae and specify the compounds

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already identified in isoprene-derived SOA.

Page 11, lines 13-14. It is confusing. They are particle phase products. As written it can be understood that 2MT and 2MG are formed in the gas phase as secondary products. In addition, 2-MT should be a tertiary product not a secondary. ISO→ISOPOOH→IEPOX→2-MT

Page 12, lines 1-17. Need to use it to compare quantification. While the authors mentioned that the detailed analysis was performed using LC-MS in positive and negative modes, only the negative mode is presented in this study, why?

The authors could have used the benefit of deploying two complementary techniques by comparing the concentrations obtained from both methods. But instead, they are giving qualitative data and do not seem to be eager to tackle the "analytical limitations" (page 15, line 6). The authors need to revise their analytical methods and use the full potential of the methods used in this study: - Comparison LC/ESI(-)-MS vs GC need to be proposed for the acids using similar standards. - Comparison LC/ESI(+)-MS vs GC need to be proposed for the polyols using similar standards. - Additional standards commercially available (e.g. erythritol, organosulfate. . .) can be used. Indeed the authors used only one acid to quantify a wide range of compounds. What can be the impact? - Which fraction of the SOA can be explained by the compounds identified in the different experiments?

What does the relative abundance mean? Is it normalized by the volume of air collected? The authors mentioned that they did not quantify the organosulfates but in the SI the concentrations are reported...Please explain

Finally, the results presented are not well constrained. Therefore conclusions proposed based on the concentrations appear speculative: "The major SOA components detected were 2-methyltetrols, 2-methylglyceric acid and its dimer, whose maximal concentrations exceeded 800, 350 and 300 ng/m³ respectively under low-humid conditions of RH 59% (Fig. 2)."

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“Among compounds detected with LC-MS (Fig. 3), the most abundant were organosulfates derived from 2-methyltetrols (MW 216) and 2-methylglyceric acid (MW 200).”

Page 14, lines 10-12. The authors found that concentration of 2-MT increase at lower RH. It is not consistent with previous works (Lin et al., 2014 ES&T; Riva et al., 2016 ES&T). Please explain.

Page 15, Table 4. Concentration of IEPOX-1 is much higher under certain conditions. Please comment? Variability of the measurements?

Page 17, lines 10-14. What is new here? It has already been reported that acidity enhances the formation of isoprene-SOA components such as tetrols, organosulfates. Please add the references and further highlight the novelty.

Page 22, lines 13-18: How would this product be formed? Which kind of chemistry?

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