

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 #3

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Overall Comment and Recommendation:

This manuscript measures the chemical composition changes (as well as bulk SOA yields) of isoprene SOA produced under acidic and non-acidic conditions as a function of relative humidity. The kind of results presented here could certainly be of value to the atmospheric and aerosol research communities. However, as I will stress in some of my major comments below, I think one thing that is missing is a stronger connection to current models that explicitly predict isoprene SOA formation through acid-catalyzed multiphase chemical processes. Of these processes, the acid-catalyzed multiphase chemistry of IEPOX on acidic (and wet) sulfate aerosol has been shown to be one

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of the dominant sources of isoprene SOA in atmospheric PM samples (e.g. Claeys et al., 2004, Science; Lin et al., 2013, ACP; Budisulistiorini et al., 2015, ACP, etc. etc.). The acid-catalyzed multiphase chemistry of high-NO_x SOA precursors, such as HMML/MAE, have been shown to yield very little SOA in atmospheric PM samples (e.g., Lin et al., 2013, ACP; Budisulistiorini et al., 2015, ACP; Rattanavaraha et al., 2016, ACP). Since IEPOX has been shown to be so important to forming SOA in atmospheric PM samples, recent work has been really aimed at measuring reactive uptake (or multiphase chemical) kinetics of IEPOX on differing aerosol types as a function of aerosol acidity and RH (Gaston et al., 2014, ES&T; Riedel et al., 2015, ES&T Letters). Recently, how RH affects both aerosol acidity and aerosol-phase state (morphology) has been examined to determine how the reactive uptake kinetics changes (Zhang et al., 2018, ES&T Letters). These studies have helped to further develop models, such as CMAQ (Pye et al., 2013, ES&T), GAMMA (McNeill 2015, ES&T), and GEOS-Chem (Maraias et al. 2016, ACP), that now explicitly predict 2-methylterols and organosulfates derived from the acid-catalyzed multiphase chemistry of IEPOX as well as predicting 2-methylglyceric acid and organosulfates derived from multiphase chemistry of MAE/HMML. Since there are now models to predict many of the SOA constituents you measure here, I think you need to present your data in a clearer way in how this can improve future modeling efforts. This is a major shortcoming of the present work and why I strongly suggest this manuscript requires revision before full publication in ACP can be considered.

Another major problem with this manuscript is it is poorly written in many sections (including grammar issues and improper citations) and fails to connect their results to recent advances on isoprene SOA chemistry. I've made suggestions below in the major comments section on how some of this can be improved. One of the authors who is a native English speaker should really carefully review the written text for these authors before resubmitting the revised draft. I found the poor writing distracting while reading the manuscript.

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Major Revisions:

- 1.) Page 2, Lines 4-6: Best to cite Guenther et al. 2006, Guenther et al., 1995 for this sentence and remove its citation in the first sentence. Along with the Goldstein and Galbally (2007) in the first sentence (lines 2-4), the authors could cite Hallquist et al. (2009, ACP).
- 2.) Page 2, Lines 8-10: Again, greater care is needed with this sentence! 2-methyltetrols, 2-methylglyceric acid, and organosulfates all form from multiphase chemistry and NOT gas-phase oxidation chemistry. However, I think the authors mean to say that certain oxidation products from isoprene + OH, isoprene + NO₃, or isoprene + O₃ undergo subsequent multiphase chemical reactions to yield these important SOA constituents.
- 3.) Page 2, Line 12: correct the spelling of "Clayes" here.
- 4.) Page 2, Line 18: Probably worth citing Surratt et al. (2006, JPCA) and Surratt et al. (2010, PNAS) for the NO_x concentration having an affect on the isoprene SOA composition.
- 5.) Page 2, Lines 22-24: Citations to the published literature are needed for this sentence.
- 6.) Page 2, Lines 24-26: The authors need to also include the fact that the acid-catalyzed multiphase chemistry (or reactive uptake) of IEPOX also highly depends on the aerosol phase state. As recently shown by Zhang et al. (2018, ES&T Letters) the reactive uptake of IEPOX is adversely affected if aqueous sulfate aerosol is coated with viscous SOA. This causes a substantial diffusion barrier that the IEPOX can't react in the aqueous acidic core. This recent work is also supported by initial findings presented in Gaston et al. (2014, ES&T) and Riva et al. (2016, ES&T).
- 7.) Page 2, Line 26-27: Acid-catalyzed reactions of isoprene ozonolysis products have also been recently reported by Riva et al. (2015, Atmos. Environ.) and Riva et al.

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(2017, Atmos. Environ.). These are worth mentioning here.

8.) Page 3, Line 5: Don't the authors mean Surratt et al. (2007, ES&T) and not Kleindienst et al. (2007)? This seems strange to me.

9.) Chemical Artifacts (Potentially Serious Issue):

Since filters were collected and extracted and derivatized for GC/EI-MS, can the authors comment on any potential artifacts? The reason this is so important is that recent work by Lopez-Hilfiker et al. (2016, ES&T) showed that IEPOX-derived SOA had a much lower volatility than expected. It turned out that they provided evidence that 2-methyltetrols and C₅-alkene triols are likely thermal degradation products from accretion products (oligomers and organosulfates). Can the authors rule out that these novel GC/MS products are not simply thermal degradation products of accretion products found with the SOA?

10.) Page 5, Lines 23-28: How were OC and SO₂ emissions estimated from the Poland sites? This needs to be clarified in the experimental section.

11.) Table 1: It would be easier if you could label on Table 1 what the sulfate mass concentrations were in there. Also, why didn't the authors consider running a thermodynamic model like ISORROPIA to estimate aerosol acidity. That way you can estimate what the aerosol acidity is as a function of RH. Obviously, as RH is increasing it is adding more water to your particles that you atomize the same way at each test condition, and thus, your pH is becoming less acidic.

12.) Page 8, Lines 3-5: Citations are warranted to prior studies that characterized these ions as characteristic ions for organosulfates and nitrooxy organosulfates.

13.) IEPOX-1 and IEPOX-2 is VERY STRANGE:

IEPOX-1 and IEPOX-2 don't make any sense to me. Do the authors mean they are the isomers of 3-MeTHF-3,4-diols? These were first characterized by authentic standards in Lin et al. (2012, ES&T) by the Surratt Group at UNC. 3-MeTHF-3,4-diols have similar

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retention times as those shown here in the present study. I'm very confused by this.

14.) Table 2 - LC/MS section:

MW 230 is the wrong structure. I'm surprised by the carelessness here.

15.) Page 11, Lines 19-20: You're specific about the other tracers precursors (i.e., IEPOX and MPAN). Why not be more specific here for these recently reported new SOA tracers?

16.) Page 12, Lines 13-14: What are the uncertainties of using ketopinic acid to quantify all eight isoprene SOA constituents measured by GC/EI-MS?

17.) Page 12, Lines 16-17: The fact that you measure 2-methyltartaric acid organosulfate at levels above baseline in your LC/ESI-MS makes me wonder how important this compound really is to isoprene SOA formation. More specifically, what is the exact precursor to this species that forms from the gas-phase oxidation of isoprene?

18.) Page 14, Lines 5-7: The terminology "the most abundant were organosulfates derived from 2-methyltetrols (MW 216) and 2-methylglyceric acid (MW 200)" is incorrect. This should really state "Organosulfate monomers derived from acid-catalyzed multiphase chemistry of IEPOX (MW 216) and MAE/HMML (MW 200)" to more accurately reflect their sources (Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T; Lin et al., 2013, PNAS; Nguyen et al., 2015, PCCP). For the IEPOX-derived organosulfates, they are being termed 2-methyltetrol sulfates and 3-methyltetrol sulfates to reflect the possible isomers that form from the multiphase chemistry of the IEPOX isomers (i.e., cis- and trans-beta-IEPOX and delta-IEPOX). Recall, Bates et al. (2014, JPCA) showed that the cis- and trans-beta-IEPOX isomers are the predominant isomers that form in the gas phase, with trans-beta-IEPOX being the most abundant. The beta-IEPOX isomers likely lead to the 2-methyltetrol sulfate isomers.

19.) Page 14, Lines 17-18: I'm not in agreement with this statement. Precursors for organosulfates typically form in the gas phase from the oxidation of isoprene. Such

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precursors like IEPOX have large Henry's law constants, and thus, can partition into any aerosol water that might be present in the aerosol phase. Thus, the detection of these organosulfates could simply result from the fact that there is enough water on these particles (especially if organics condense and then take up water). I think the authors are unable to rule out this possibility based on their data.

20.) The ER labelling of experiments is really not helpful to readers. Can't you simply just call one set of experiments the acidic experiment at varying RH and the other one the non-acidic experiment at varying RH?

21.) As shown in Table 4 heading, reporting $[H^+]_{air}$ concentration isn't really helpful to modeling. Couldn't the authors use one of the thermodynamic models to estimate what the INITIAL pH is of these particles? If the authors recall, McNeill (2015, ES&T), Pye et al. (2013, ES&T) and Maraias et al. (2017, ACP) have developed explicit models to predict IEPOX SOA. These models have been further developed by aerosol flow tube reactors that determine the reactive uptake coefficient of IEPOX as a function of acidity (Gaston et al., 2014, ES&T; Riedel et al., 2015, ES&T Letters), RH (Gaston et al., 2014, ES&T; Zhang et al., 2018, ES&T Letters) and pre-existing SOA coatings (Gaston et al., 2014, ES&T; Zhang et al., 2018, ES&T Letters). It's not clear to me how this data you show in Table 4 and Table 3 can help improve explicit modeling of many of these SOA products. The GAMMA, CMAQ, and GEOS-Chem models all now explicitly predict 2-methyltetrols and the organosulfates derived from the acid-catalyzed chemistry of IEPOX. In addition, some of these models, like CMAQ, now predict 2-methylglyceric acid and the organosulfate derived from MAE/HMML multiphase chemistry. I think much more care is needed by the authors to convince readers and reviewers how this data can be used to further improve these much needed models. I strongly believe these models have to explicitly model the acid-catalyzed multiphase chemistry of isoprene oxidation products that consider the interconnecting effects of aerosol acidity and aerosol phase state, which both depend on the RH condition.

22.) Figure 4 is poorly generated. Too difficult to read. Please regenerate this figure.

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Why do some figures use color and others use black and white. I think your figures need to be more consistently generated.

23.) Figure 6: It remains unclear to me how much sulfate was present in all the conditions shown in this figure, the tables of the experimental conditions, and the experimental description. Is sulfate the same concentration in each experiment? 2-MG has been shown to be reduced in concentration if the acidity of the aerosol is high (Nguyen et al., 2015, PCCP). In fact, there is prior evidence that the nucleation of 2-MG and its corresponding oligoesters is enhanced under dry conditions (Nguyen et al., 2011, ACP; Zhang et al., 2011, AcP). I wonder, do you have evidence in your size distribution measurements of nucleation events? I ask this since it appears your sulfate seed aerosol concentrations were quite low at the start of each experimental condition.

24.) Surratt et al. (2007, ES&T) - The authors don't compare their results to that paper. That paper showed 2-MG concentration doesn't change with increasing aerosol acidity, but the 2-methyltetrols do.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-273>, 2018.