

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

Response to reviewer’s comments (# 3)

This reviewer said in the general comments:

“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 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.**”

Response. First, we would like to thank this reviewer for the time and effort spent in reading and evaluating this manuscript. While the results presented in this paper could certainly benefit from additional information regarding modeling work, we do not believe that this information is vital to the comparisons presented. Although, we do agree with the reviewer's assessment of the importance of modeling.

Multiphase chemistry (e.g. relative uptake of IEPOX on aerosol particles) has been shown to be important in forming SOA in atmospheric PM samples (e.g. Gaston et al., 2014; Riedel et al., 2015), and as noted in our response to reviewer # 2, comment # 20, it is important to measure directly or have an accurate estimate of aerosol liquid water content in order to accurately "model" the formation of isoprene reaction products formed under a wide range of RH. Liquid water inorganic species measurements were not available for this study. Air quality modeling to improve organic PM predictions using the organic markers as constraints is both outside the scope of this paper and, in any case, is not at the stage to help improve model results. How such modeling might function is given in the last paragraph of the Results and Discussion.

We have added now the following paragraph to address this issue just before the Summary section in the revised manuscript:

"While these experiments provide an analysis of a wide range of isoprene reaction products in the aerosol phase as a function of RH and acidity, they also include a number of shortcomings that need to be addressed in future work. Perhaps the most significant is the use of authentic standards to assess the contribution of these products to SOA mass at different RH. In addition, when the relative humidity is varied, it is important to measure aerosol liquid water content directly or estimated using thermodynamic models, such as ISOPROPIA (Fountoukis and Nenes, 2007) or AIM (Wexler and Clegg, 2002), and other gas and particle composition (e.g. inorganic species). Liquid water inorganic species measurements were not available for this study.

"The use of these marker compounds for ambient air quality models can follow the approach of Pye et al. (2013). In such an approach, the model is run using a base case chemical mechanism for isoprene, where there is no adjustment for acidity and relative humidity. A comparison can then be made with the same model having such an adjustment incorporated within the isoprene mechanism provided that absolute concentrations can be assigned. The markers can then serve as constraints to the PM observations. For the U.S. the Community Multiscale Air Quality (CMAQ) model is frequently used for ozone and PM ambient concentrations (Pye et al., 2013). For Poland, a similar approach can be used with a European model having the appropriate meteorology and chemical mechanism (Miranda et al. 2015)."

The reviewer goes on to say”

“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.”

Response. The revised manuscript was carefully edited for appropriate scientific-English terminology as well as to explicate certain sections or paragraphs that may have lacked clarity or been perplexing. The results have been augmented to reflect recent advances in isoprene SOA chemistry.

Major revisions.

Comment #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).”

Response. This was corrected as suggested by the reviewer. Guenther et al., 2006 was added to the reference section.

Comment #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.”

Response. We did not understand the reviewer concerns here. We refer to isoprene removal through gas phase chemistry and not to its oxidation products. We agree somewhat with the reviewer that 2- methyltetrols, 2- methylglyceric acid, and organosulfates are formed only through multiphase chemistry but we cannot exclude their gas phase formation also, at least for the 2-methyltetrols and 2-methylglyceric acid. For examples, 2- methyltetrols and 2-methylglyceric acid were detected in our laboratory in the gas phase from the chamber

oxidation of isoprene and as indicated in the associated mechanism (Kleindienst et al., 2009). Our chamber data are consistent with isoprene oxidation products 2-methyltetrols and 2-methylglyceric acid presence either in the gas phase, in the particle phase, or both. 2-Methyltetrols were also reported in ambient samples in the gas phase (Xie et al., 2014). During a recent inter-comparison study during 2013 SOAS field study, using four “real-time” instruments (FIGAERO-HRToF-CIMS with acetate ionization source; FIGAERO-HRToF-CIMS with iodide ionization source; semi-volatile thermal desorption aerosol GC-MS (SV-TAG); high-resolution thermal desorption proton-transfer reaction mass spectrometer (HR-TD-PTRMS)) for gas/particle partitioning of organic species, Thomson et al. (2016) show the difficulties of these instruments in the interpretation of complex ambient samples. Note that the formation of 2-methyltetrols and 2-methylglyceric acid and other isoprene/momoterpene products in the gas or particle phase through multiphase chemistry remain poorly constrained.

However, to reflect the reviewer comment, we changed the following sentences from:

“The primary removal of ISO in the atmosphere is through the gas-phase reactions with hydroxyl radicals (OH), nitrate radicals (NO₃) and ozone (O₃) which result in the formation of numerous oxidized SOA components, including 2-methyltetrols, 2-methylglyceric acid, C₅-alkene triols and C₄/C₅ organosulfates (OSs). These compounds were identified in ambient PM_{2.5} (particulate matter with diameter < 2.5 μm) in several places around the world while SOA generated from isoprene was reported to account for up to 20 – 50% of the overall SOA budget (Clayes et al., 2004a; Wang et al., 2005; Henze and Seinfeld, 2006; Kroll et al., 2006; Surratt et al., 2006; Hoyle et al., 2007).” which is changed to:

“The primary removal mechanism for isoprene is by gas-phase reactions with hydroxyl radicals (OH), nitrate radicals and, to a lesser extent, ozone. These processes result in the formation of gas and aerosol products include numerous oxidized SOA components. Aerosol species reported including 2-methyltetrols, 2-methylglyceric acid, C₅-alkene triols and organosulfates (OSs) (i.e. Edney et al., 2005; Surratt et al., 2007a, 2010; Riva et al., 2016; Spolnik et al., 2018). While many of these are formed through multiphase chemistry (e.g. IEPOX channel), we cannot exclude their gas phase formation at least for 2-methyltetrols and 2-methylglyceric acid, as these compounds have been linked to gas phase reaction products from the oxidation of isoprene (Kleindienst et al., 2009) and in ambient PM_{2.5} (Xie et al., 2014). Moreover, these compounds were identified in ambient PM_{2.5} in several places around the world, and SOA from isoprene often accounts for 20–50% of the overall SOA budget (Clayes et al., 2004a; Wang et al., 2005; Henze and Seinfeld, 2006; Kroll et al., 2006; Surratt et al., 2006; Hoyle et al., 2007).”

The following references were added to the reference section.

Mingjie X., Hannigan M.P. and Barsanti K.C.: Gas/Particle Partitioning of 2-Methyltetrols and Levoglucosan at an Urban Site in Denver, *Environ. Sci. Technol.*, 48, 2835–2842, 2014.

Kleindienst T.E., Lewandowski M., Offenberg J.H., Jaoui M. and Edney E.O.: The formation of secondary organic aerosol from the isoprene + OH reaction in the absence of NO_x, *Atmos. Chem. Phys.*, 9, 6541–6558, 2009.

Thompson S.L., Reddy L.N. Yatavelli, Harald Stark, Joel R. Kimmel, Jordan E. Krechmer, Douglas A. Day, Weiwei Hu, Gabriel Isaacman-VanWertz, Lindsay Yee, Allen H. Goldstein, M. Anwar H. Khan, Rupert Holzinger, Nathan Kreisberg, Felipe D. Lopez-Hilfiker, Claudia Mohr, Joel A. Thornton, John T. Jayne, Manjula Canagaratna, Worsnop D.R. and Jimenez J.L: Field intercomparison of the gas/particle partitioning of oxygenated organics during the Southern Oxidant and Aerosol Study (SOAS) in 2013, *Aerosol Sci. Technol.*, 51, 30-56, 2017.

Comment #3. “Page 2, Line 12: correct the spelling of "Claeys" here.”

Response. We thank the reviewer for this. This has been corrected.

Comment #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”

Response. This was updated as suggested by the reviewer.

Comment #5. “Page 2, Lines 22-24: Citations to the published literature are needed for this sentence.”

Response. To reflect the reviewer comment, we added the following references on page 2, line 24 (original manuscript): (Lin et al., 2013; Budisulistiorini et al., 2016; Rattanavaraha et al., 2016; Gaston et al., 2014; Riedel et al., 2015; Zhang et al., 2018).

These new references were added to the revised manuscript.

Lin Y.-H., Knipping E. M., Edgerton E. S., Shaw S. L., and Surratt J. D.: Investigating the influences of SO₂ and NH₃ levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches. *Atmos. Chem. Phys.*, 13, 8457–8470, 2013.

Budisulistiorini S.H., Baumann K., Edgerton E.S., Bairai S.T., Mueller S., Shaw S.L., Eladio M. Gold K.A. and Surratt J.D.: Seasonal characterization of submicron aerosol chemical composition and organic aerosol sources in the southeastern United States: Atlanta, Georgia, and Look Rock, Tennessee, *Atmos. Chem. Phys.*, 16, 5171–5189, 2016.

Zhang Y., Chen Y., Lambe A.T., Olson N.E., Lei Z., Craig R.L., Zhang Z., Gold A., Onasch T.B., Jayne J.T., Worsnop D.R., Gaston C.J., Thornton J.A., Vizuete W., Ault A.P. and Surratt J.D.: Effect of the Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX), *Environ. Sci. Technol. Lett.*, 5, 167–174, 2018.

Rattanavaraha, W., Chu, K., Budisulistiorini, S. H., Riva, M., Lin, Y.-H., Edgerton, E. S., Baumann, K., Shaw, S. L., Guo, H., King, L., Weber, R. J., Neff, M. E., Stone, E. A., Offenberg, J. H., Zhang, Z., Gold, A. and Surratt, J. D.: Assessing the impact of anthropogenic pollution on isoprene-derived secondary organic aerosol formation in PM_{2.5} collected from the Birmingham, Alabama, ground site during the 2013 Southern Oxidant and Aerosol Study, *Atmos. Chem. Phys.*, 16, 4897–4914, 2016.

Gaston C. J., Thornton J. A. and Ng N. L.: Reactive uptake of N₂O₅ to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations, *Atmos. Chem. Phys.*, 14, 5693-5707, 2014.

Riedel T. P., Lin Y-H., Budisulistiorini S. H., Gaston C. J., Thornton J. A., Zhang Z., Vizuete W., Gold A., and Surratt J. D. : Heterogeneous Reactions of Isoprene-Derived Epoxides: Reaction Probabilities and Molar Secondary Organic Aerosol Yield Estimates, *Environ. Sci. Technol. Lett.*, 2, 38–42, 2015.
Riedel et al., 2015.

Comment #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*).”

Response. We added the following sentences to the revised manuscript on page 2, line 25 (original manuscript) and read:

“However, this type of multiphase chemistry following the uptake of IEPOX can be highly

dependent on the aerosol phase state and the presence of aerosol coatings from viscous SOA constituents (Zhang et al., 2018). Such coatings can cause a substantial diffusion barrier to the availability to an acidic core.”

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

Response. We have added the Riva et al., 2016 (we believe the reviewer is referring to 2016 Riva et al. paper and not to a 2015 paper) and Riva et al., 2017 references to the revised manuscript.

Riva, M., Budisulistiorini, S.H., Zhang, Z., Gold, A. and Surratt, J.D.: Chemical characterization of secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol. Atmos. Environ. 130, 5-13, 2016.

Riva M., Budisulistiorini S.H., Zhang Z., Gold A., Thornton J.A., Turpin B.J. and Surratt J.D.: Multiphase reactivity of gaseous hydroperoxide oligomers produced from isoprene ozonolysis in the presence of acidified aerosols. Atmos. Environ. 152, 314-322, 2017.

Comment #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.”

Response. This is corrected as suggested by the reviewer.

Comment #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?”

Response. Artifact peaks associated with silylation (BSTFA) derivatization elute early in the chromatogram and are clearly recognizable from isoprene oxidation products (e.g. by the interpretation of their mass spectra and their occurrence in blank and background samples), which elute after artifact peaks. In addition, BSTFA

artifacts were identified in our work by acquiring blank and/or background chamber, as well as from analyzing about a hundred of standards derivatized in our laboratory, including methyltetrols, and IEPOX.

The point brought by the reviewer associated with accretion products is very important. Lopez-Hilfiker et al. (2016) analyzing samples collected during the 2013 SOAS field study, hypothesize that 2-methyltetrols and C5-alkene triols *are likely thermal decomposition* products from accretion products. These authors analyzed thermograms originated from filters collected on FIGAERO-CIMS system (PM1), and measured the bulk aerosol composition. The possibility of artifacts in our methods or in the FIGAERO-CIMS must always be recognized, and they are typically checked but not necessarily reported. In prior work, we have addressed possible sample handling problems and do not believe that further work is required on our behalf. We feel that the potential issues using the CIMS-FIGAERO instrument might need further exploration to address that instrument-specific formation artifacts and analyte losses (e.g. thermal decomposition, using vacuum and its effect on more volatile compounds losses).

Our data provide strong evidence that 2-methylglyceric acid, 2-methyltetrols and C5-triols exist in our systems as monomers as well as dimers. (See compounds observed as dimer in the figures below as well as Jaoui et al., 2008). The derivatization technique used in this study is not associated with thermal decomposition as speculated by Lopez-Hilfiker et al. (2016). As an example, the figure below shows the presence of monomers: 2-methylglyceric acid and 2-methyltetrols as monomers as well as and dimers (2-methyltetrols_2-methylglyceric acid dimers) in the same or similar system (Jaoui et al. 2008; also SOA from isoprene + ozone). This is consistent that silylation reactions does not leading to isoprene dimers through thermo-decomposition by the extraction and derivatization procedure given that we detect dimers and monomers as TMS-derivative. In addition, we conducted two derivatizations on isoprene SOA extract using the same amount of the extract for each derivatization. Both derivatizations underwent the same steps except one was heated to 70 °C for 1 hour (same technique used in this study), and the second was left for 24 hours at room temperature (no heat). The results show that chromatograms acquired from both derivatization were essentially identical, confirming that the BSTFA derivatization does not lead to thermal decomposition of the TMS-dimer isoprene products. In fact, the silylation derivatization can be a useful tool for identifying the presence of oligomers in SOA as shown in the figure.

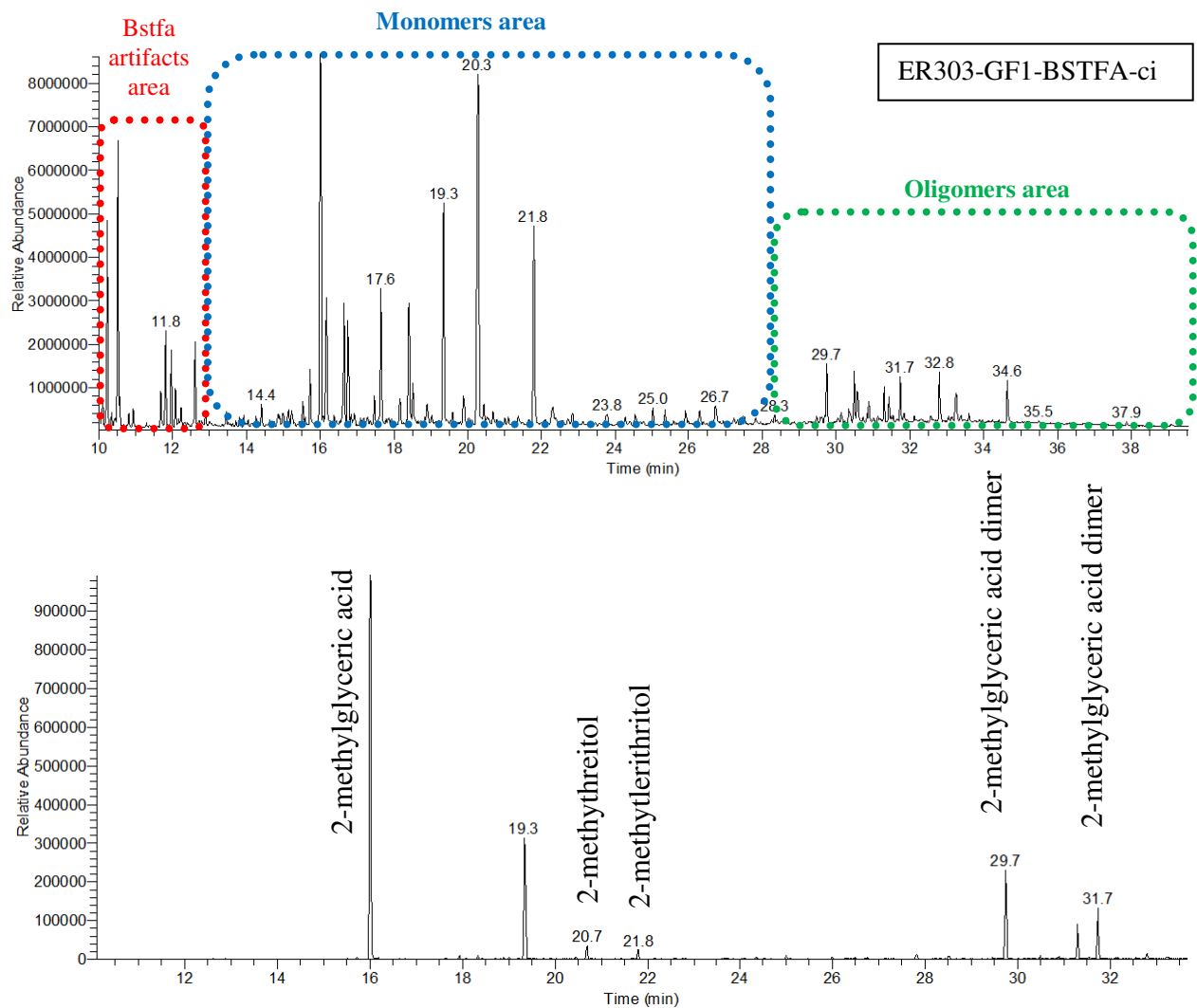
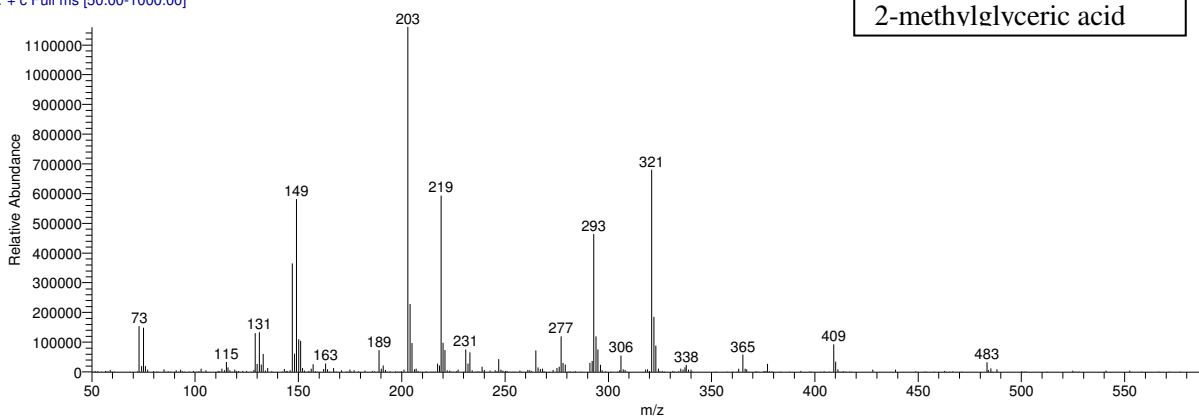


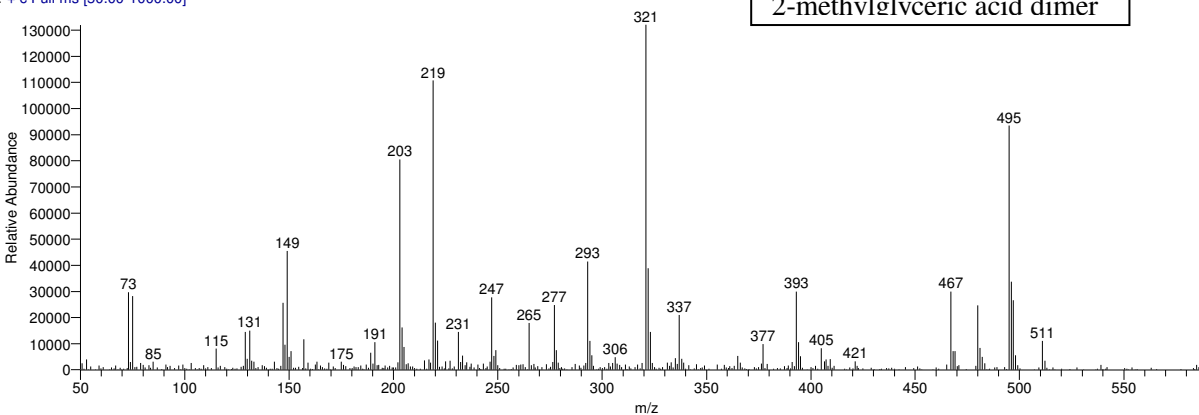
Figure 1. Total (top) and extracted (bottom) ion chromatograms of an isoprene ozone experiment showing the presence of monomeric and dimers oxidation products using silylation reaction (BSTFA) using the same protocol used in the paper.

ER303-GF1-BSTFA-ci #432 RT: 16.00 AV: 1 NL: 1.16E6
T: + c Full ms [50.00-1000.00]



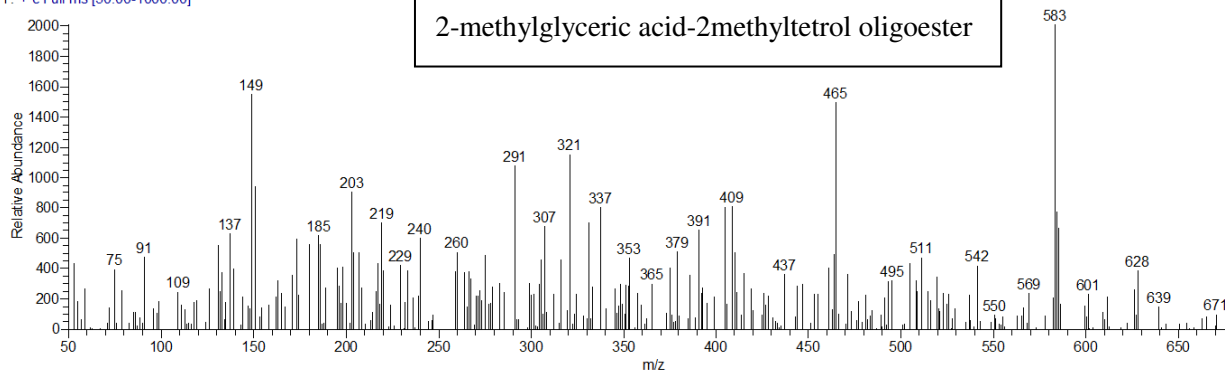
2-methylglyceric acid

ER303-GF1-BSTFA-ci #1413 RT: 29.75 AV: 1 NL: 1.32E5
T: + c Full ms [50.00-1000.00]



2-methylglyceric acid dimer

ER303-GF1-BSTFA-ci #1583 RT: 32.16 AV: 1 SB: 10 32.32-32.38, 31.99-32.05 NL: 2.01E3
T: + c Full ms [50.00-1000.00]



2-methylglyceric acid-2-methyltetrol oligoester

Figure 2. Mass spectra associated with isoprene monomer 2-methylglyceric acid and dimers observed simultaneously in isoprene SOA.

Comment #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.”

Response. We changed “section 2.2.” to reflect the reviewer comments and read:

“Twenty ambient PM_{2.5} samples were collected, onto pre-baked quartz filters using a high-volume aerosol sampler (DH-80, Digitel), from two sites (ten samples each) having strong isoprene emissions: (1) a regional background monitoring station in Zielonka, in the Kuyavian-Pomeranian Province in the northern Poland (PL; 53°39' N, 17°55' E) during summer 2016 campaign, and (2) a regional background monitoring station in Godow, PL located in the Silesian Province (49°55' N, 18°28' E) in summer 2014 campaign. Sampling times were 12 and 24 hours, respectively. Major tree species at both sites are European oak (*Quercus robur* L.); European hornbeam (*Carpinus betulus* L.); Tilia cordata (Tilia cordata Mill); European white birch (*Betula pubescens* Ehrh); and European alder (*Alnus glutinosa* Gaertn). The Zielonka station is in a forested area while the Godow station is located near a coal-fired power station in Detmarovice (Czech Republic). Godow is also close to the major industrial cities of the Silesian region in Poland, and thus aerosol samples collected in Godow were influenced by anthropogenic sources.

Several chemical and physical parameters were measured at the two sites. The relative humidity during sampling was up to 86% in Zielonka and 94% at Godow. Both locations were influenced by NO_x concentration, modestly in Zielonka at 1.3 µg m⁻³ and at a level of 30 µg m⁻³ in Godow, represented by the nearest monitoring station at Zywiec, PL. The SO₂ levels at Zielonka were approximately 0.6 µg m⁻³ and 3.0 µg m⁻³ at Godow. At each site, OC/EC values was determined for each filter using a thermo-optical method (Birch and Cary, 1996). The organic carbon value at Zielonka was approximately 1.7 µg m⁻³ and 5.4 µg m⁻³ at Godow, although aerosol masses were not determined.”

Comment #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.”

Response. To address the reviewer comment, we updated the caption of Table 1, and now reads:

“**Table 1.** Initial and steady state conditions, yields and OM/OC data for chamber experiments on isoprene

photooxidation in the presence of acidic and non-acidic seed aerosol. The initial NO_x was entirely nitric oxide. Experiment ER667 was conducted at a low-concentration ammonium sulfate seed (~1 μg m⁻³). Experiment ER662 was conducted with a higher concentration of inorganic seed (~30 μg m⁻³) generated from a nebulized solution for which half the sulfate mass was derived from sulfuric acid and the other half from ammonium sulfate (Lewandowski et al., 2015). As for using thermodynamic models for aerosol acidity, see the responses to reviewers from Lewandowski et al., 2014, and our response to reviewer # 2, comment 20. A copy of Lewandowski et al. 2015 response to similar comment is provided below and reads:”

“In the varied RH experiments, where [H⁺]_{air} measurements are of limited value (since the maximum dissociated H⁺ in the extracts remains unchanged, but actual aerosol pH is expected to change with liquid water content), we agree with the reviewer that aerosol pH levels or aerosol liquid water concentrations would be of tremendous value to the interpretation of the results. Unfortunately, we do not have sufficient composition information to do the modeling with ISORROPIA or AIM appropriately. While chamber temperature, RH, and particle sulfate loading are known for each reaction step, particle phase ammonium and nitrate were not measured in these experiments. And, although not strictly necessary, no gas-phase ammonia or nitric acid concentrations are available (and, as high-NO_x experiments, nitric acid concentrations should be non-trivial), further complicating model predictions. Additionally, as with the SOAS field measurements reported in Guo et al., 2014, we have a significant aerosol fraction composed of isoprene-related organic aerosol to contend with, which can further contribute to aerosol phase water content, but is not accounted for in the models. Given these limitations, we believe that any modeled pH levels or aerosol liquid water concentrations that we could generate from our existing data would be suspect and potentially counterproductive to the analysis (due more to our under-analysis of the aerosol composition than to any limitations inherent in the models). While we readily admit that humidity provides, at best, an indirect measure of the physically important aerosol parameters of interest in these comparisons, it is nevertheless the most reliable measurement surrogate that we have to work with in this data set.”

See our response to reviewer 2, comment # 20 for additional text added to the revised manuscript.

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

Response. We added the following references.

Darer, A.I., Cole-Filipiak N.C., O'Connor A.E. and Elrod M.J.: Formation and stability of atmospherically relevant isoprene-derived organosulfates and organonitrates. *Environ. Sci. Technol.* 45, 1895-1902, 2011.

Szmigielski, R., Evidence for C₅ organosulfur secondary organic aerosol components from in-cloud processing of isoprene: Role of reactive SO₄ and SO₃ radicals, *Atmos. Environ.* 130, 14-22, 2016.

Comment #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.”

Response. We are not sure what the reviewer is referring here. IEPOX-1 and IEPOX-2 are defined in Table 2 with their structure and nomenclature. These compounds are reported in the literature during the last six years and are isomers of 3-MeTHF-3,4-diols. To reflect the reviewer comment, we added Lin et al., 2012 reference to the revised manuscript.

Lin Y.-H., Zhang Z., Docherty K.S., Zhang H., Budisulistiorini S.H., Rubitschun C.L., Shaw S.L., Knipping E.M., Edgerton E.S., Kleindienst T.E., Gold A., Surratt J.D.: Isoprene Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed Reactive Uptake Studies with Authentic Compounds, *Environ Sci Technol.*, 3, 46, 250–258, 2012.

Comment #14. “Table 2 - LC/MS section: MW 230 is the wrong structure. I’m surprised by the carelessness here.”

Response. We thank the reviewer. This was corrected.

Comment #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?”

Response. See response to comment 15, reviewer # 2.

Comment #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?”

Response. Due to lack of authentic standards, we used ketopinic acid for all samples, as we have in past studies, to estimate the changes associated with each compound reported in this study as the RH or acidity changes. As noted in Figures 2, 4, Tables 3, 4 captions, these are necessarily estimates. Without authentic standards, it is difficult to estimate the uncertainties of using ketopinic acid. (See Jaoui et al., (2005) for a further discussion of this point.

Comment #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?”

Response. See our response to comment #15, reviewer #2.

Comment #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.”

Response. The whole paragraph (page 14, line 4-14: original manuscript was updated and now reads:

" The major SOA components detected were 2-methyltetrols, 2-methylglyceric acid and its dimer, whose maximal estimated concentrations exceeded 800, 350 and 300 ng m⁻³ respectively under low-humid conditions of RH 9% (Figure 2). Among compounds detected with LC-MS (Figure 3) are organosulfates derived from acid-catalysed multiphase chemistry of IEPOX (MW 216) and MAE/HMML (MW 200) (Surratt et al., 2010; Lin et al., 2012, 2013; Nguyen et al., 2015). Other components were significantly less abundant. In most cases, increasing the RH resulted in decreased yields of the products detected, although some compounds were observed at higher concentrations at RH 49% compared to RH

9% (i.e. m/z 199: Figure 3). Total SOC decreased with increased RH (Table 1). Generally, the influence of RH on the product yields was mild, with the exception of 2-methyltetrols, 2-methylglyceric acid, and 2-methylglyceric acid dimer which were produced in significantly larger amounts at RH 9% compared to RH 49%. This is generally consistent with Dommen et al. (2006) and Nguyen et al. (2011), who saw a negligible effect of relative humidity on SOA formation in photooxidation of isoprene in the absence of acidic seed aerosol. Two recent studies (Lin et al., 2014; Riva et al., 2016) reported an increase in aerosol mass with increasing RH. Riva et al., (2016) reported also an increase in 2-methyltetrols concentrations with increasing RH. These two studies were fundamentally different than those in the present study. In our study, isoprene was oxidized in the presence of NO_x and seed aerosol (acidic and non-acidic) under a wide range of humidity, however hydroxyhydroperoxide (ISOPOOH), and IEPOX were used as reactant in Riva et al., and Lin et al. studies under two RH and free-NO_x conditions.”

Comment #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 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.”

Response. In our sentence on page 14, lines 17-19 that reads “However, organosulfates were also formed in non-acidic experiments, probably through radical-initiated reactions in wet aerosol particles containing sulfate moieties (Nozriere et al., 2010; Perri et al., 2010). The NOS and OS compounds we detected could also occur *via* this mechanism.”

We did not understand the reviewer concerns here. We refer in this sentence to the formation of organosulfates in the non-acidic seed aerosol and how they may be formed, that is, from where the sulfate group originates. We do agree with the reviewer that IEPOX may be a precursor to these organosulfates in the non-acidic aerosol.

Comment #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?”

Response. The ER label is associated with the chamber used to generate these data. Therefore, for quality assurance purposes and clarity these labels were kept in the revised manuscript, when appropriate. We do not feel this is too distracting for the reader.

Comment #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.”

Response. We generally agree with the reviewer’s assessment of the limitations of the [H+] air measurement. See our response to comment # 11 above for running a thermodynamic model to estimate the initial pH. Also see our comment to reviewer # 2, comment # 20.

Comment #22. “Figure 4 is poorly generated. Too difficult to read. Please regenerate this figure. Why do some figures use color and others use black and white. I think your figures need to be more consistently generated.”

Response. This figure is regenerated as shown in the revised manuscript. All figures in the revised manuscript are now consistent.

Comment #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.”

Response. See our response to Comment #11 above for sulfate concentrations associated with both experiments. Sulfate concentrations are internally consistent within each experiment, but the two runs use both different inorganic concentrations and different inorganic compositions, as noted in our response to comment #11. See the experimental section of Lewandowski et al. (2015) for additional text describing the experimental conditions. As all experiments start with non-trivial concentrations of inorganic material (at least one-third of the total particle mass in ER662, and at least 5% in ER667), would we expect any organic products formed to condense on existing inorganic particles rather than undergoing nucleation. However, as all sampling was conducted only after the chamber system reached steady-state conditions, transient nucleation events, should they somehow occur despite the presence of preexisting inorganic particles, would not be detected.

Comment #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.

Response. See our response to reviewer # 2, comment # 17.