



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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*Comments by the Editor are in blueprint, answers by the authors are in normal print

1. As both reviewers noted, this manuscript presents a thorough and comprehensive analysis, which is highly informative about the chemical details of the aerosol system investigated. Both reviewers suggested publication after minor revisions, and I agree that the article will provide valuable insight for the community on chemical processes in organic aerosol formation.

Authors' reply:

We thank the Editor for the effort to evaluate our manuscript and our response to reviewers' comments and for his positive opinion on the present manuscript.

2. However, both reviewers of this manuscript rightly pointed out that the interpretations of data trends are sometimes confusing, especially with regard to comparison between hydrated and solid seed particles. Throughout, these are referred to as "acidic" (or acidified) and "non-acidic", which is true of the solutions from which the seeds were atomized, but the far more fundamental difference between experiment sets 444 and 666 is that the particles themselves exist in different phases, which drastically changes the ability of gas-phase species to partition to the particle phase. This difference in phase is not mentioned in the abstract or conclusions; instead, there (and throughout, e.g. in sections 3.2.2 and 3.2.3), changes in the organic aerosol composition between the two experiments are attributed to particle acidity. But it cannot be stated conclusively that observed differences are "dependent on" particle acidity, as that wasn't the only difference between the 444 and 666 experiments -- phase state was as well, and these weren't separated. (Indeed it's questionable whether the non-acidified experiments can even be referred to as "less acidic" if they don't have an aqueous phase and therefore don't have a definable "acidity", so there isn't really a comparison to a less acidic solution being made.

Authors' reply:

Throughout the paper we pointed out that the aerosol aqueous phase occurred in all acidified seed experiments but was absent in all non-acidified seed experiments. However, we agree with the Editor assessment that additional details are needed, and the abstract and summary did not contain the adequate information on the phase state of aerosol particles in the two types of experiments. We also clearly clarified that between ER444 and ER666 experiments, it was the seed aerosol acidity and not the aerosol acidity which affected the formation of SOA in this system. To reflect the Editor concern, we changed the abstract from:

“This study investigated the effect of relative humidity (RH) on the chemical composition of gas and particle phases formed from the photooxidation of 1,3-butadiene (13BD) in the presence of NO_x under acidic and non-acidic conditions. The experiments were conducted in a 14.5 m³ smog chamber operated in a steady-state mode. Products were identified by high performance liquid chromatography, gas chromatography mass spectrometry and ultrahigh performance liquid chromatography coupled with high resolution mass spectrometry. More than 48 oxygenated products were identified including 33 oxygenated organics, 10 organosulfates (OSs), PAN, APAN, glyoxal, formaldehyde, and acrolein. Secondary organic aerosol (SOA) mass and reaction products were found to be dependent on RH and acidity of the aerosol. SOA mass, and most SOA products (i) were higher under acidic than non-acidic conditions, and (ii) decreased with increasing RH. Glyceric acid, threitol, threonic acids, four dimers, three unknowns, and four organosulfates were among the main species measured either under acidic or non-acidic conditions across all RH levels. Total secondary organic carbon and carbon yield decreased with increasing RH under both acidic and non-acidic conditions. The photochemical reactivity of 13BD in our systems decreased with increasing RH and was faster under non-acidic than acidic conditions. To determine the contribution of 13BD products to ambient aerosol, we analyzed PM_{2.5} samples collected at three European monitoring stations located in Poland. The occurrence of several 13BD SOA products (e.g., glyceric acid, tartaric acid, threonic acid, tartaric acid, and OSs) in the field samples suggests that 13BD could contribute to ambient aerosol formation.”

To

“This study investigated the effect of relative humidity (RH) on the chemical composition of gas and particle phases formed from the photooxidation of 1,3-butadiene (13BD) in the presence of NO_x under acidified and non-acidified seed aerosol. The experiments were conducted in a 14.5 m³ smog chamber operated in a steady-state mode. Products were identified by high performance liquid chromatography, gas chromatography mass spectrometry and ultrahigh performance liquid chromatography coupled with high resolution mass spectrometry. More than 50 oxygenated products were identified including 33 oxygenated organics, 10 organosulfates (OSs), PAN, APAN, glyoxal, formaldehyde, and acrolein. Secondary organic aerosol (SOA) mass and reaction products formed depended on RH, and acidity of the seed aerosol. Based on E-AIM modeling, the seed aerosol originated from the acidified and non-acidified solutions were found to exist under aqueous and solid phases, respectively. Although, the terms “acidified” and “non-acidified” is true for the solutions from which the seeds were atomized,

there is far more fundamental differences between the phase states in which species partition to or from (aqueous/solid), which considerably affects their partitioning and formation mechanisms. SOA mass, and most SOA products (i) were higher under acidified seed conditions, where the aerosol particles were deliquescent, than under non-acidified seed conditions, where the aerosol particles did not contain any aqueous phase, (ii) increased with the acidity of the aerosol aqueous phase in the experiments under acidified seed conditions; and (iii) decreased with increasing RH. Glyceric acid, threitol, threonic acids, four dimers, three unknowns, and four organosulfates were among the main species measured either under acidified or non-acidified conditions across all RH levels. Total secondary organic carbon and carbon yield decreased with increasing RH under both acidified and non-acidified seed conditions. The photochemical reactivity of 13BD in our systems decreased with increasing RH and was faster under non-acidified than acidified seed conditions. To determine the contribution of 13BD products to ambient aerosol, we analyzed PM_{2.5} samples collected at three European monitoring stations located in Poland. The occurrence of several 13BD SOA products (e.g., glyceric acid, tartronic acid, threonic acid, tartaric acid, and OSs) in the field samples suggests that 13BD could contribute to ambient aerosol formation.”

And we changed the summary from:

“While it is impossible to cover and analyse all reaction products associated with 13BD oxidation, this study addresses many of the main products that form under various acidity and relative humidity conditions. We identified more than 50 oxygenated organic compounds in the gas and particle phases obtained from chamber oxidation of 13BD. Some reaction products have been reported in the literature, but several others were identified for the first time: glyceric acid-organosulfate, 2(3*H*)-furanone, dihydro-3,4-dihydroxy-organosulfate (2 isomers), threonic acid-organosulfate, 1,2,3,4-butanetetrol nitrosoxy-organosulfate, 1,2,3,4-butanetetrol nitroxy-organosulfate, malic acid-organosulfate, and threonic acid nitroxy-organosulfate. The quantitative analysis showed that glyceric acid, threitol, erythritol, threonic acid, several dimers, unknowns, and organosulfates were the most abundant components of 13BD SOA under acidic and non-acidic conditions. Other components contributing to SOA mass were diols, mono- and dicarboxylic acids, organosulfates, dimers, and nitroxy- and nitrosoxy-organosulfates. Several carboxylic acids, organosulfates and nitroxy-organosulfates identified in chamber samples were also detected in ambient aerosol samples collected at various sites in Poland. Such consistency reinforces the relevance of the chamber findings even though some components were found only in chamber experiments.

Comparison between experiments conducted under acidic and non-acidic conditions at various RH revealed that both acidity and RH influenced the production of SOA as well as the number and molecular structure of products formed in the gas and particle phases. Total SOC decreased with increasing RH, but the levels of individual components varied, though the majority followed similar trends as the SOC. Ozone production and conversion efficiency of 13BD depended on RH and acidity similar to SOC. The concentrations of most compounds decreased as RH increased, but few products were most abundant at intermediate RH around 30% (e.g., malic acid, glyceric acid-OS). This is also true for gas phase formaldehyde and acrolein, whose yields increased significantly at high RH. The

acidic-seed experiments enhanced SOC production compared to non-acidic experiments under the whole RH range considered. However, at high humidity, the difference was relatively small. Yield of the individual SOA components followed the same pattern as SOC, while a few were more abundant in non-acidic experiments (e.g., unknowns) or behaved in an inconsistent manner. Further research is warranted to elucidate the mechanisms of their formation in the atmosphere. Overall, the 13BD results are consistent with those reported by Nestorowicz et al. (2018) for isoprene.

The present study employed analytical methods suitable for a wide range of 13BD reaction products in the particle and gas phases at various RH and acidity. It provided a solid identification of wide variety of reaction products including HAPs, dimers and organosulfates, as well as quantitative changes in their formation as a function of RH and acidity. Certainly, this study includes some shortcomings that need to be addressed in future work. Perhaps the most significant improvement would be the use of authentic standards to better quantify the contribution of individual products to SOA at various RH and acidity. This study shows that SOA and SOC consistently increased with decreasing RH and were higher under acidic than non-acidic conditions. Similar trends were observed for the majority of reaction products reported in this study. To assess that observation, the LWC and other thermodynamic properties of the aerosol phase were estimated as a function of RH using the thermodynamic model E-AIM.

13BD does not contribute more to atmospheric aerosol than isoprene, which is emitted to the atmosphere in a much larger amount and plays a significant role in atmospheric SOA modelling. However, 13BD emissions are less understood than isoprene, and current increases in wildfires and acreages burned due to climate issues can increase 13BD emissions and therefore the production of 13BD SOA, which may have implications for air quality, health, and well-being.”

To

“While it is impossible to cover and analyze all reaction products associated with 13BD oxidation, this study addresses many of the main products that form under various acidified and non-acidified seed aerosol and relative humidity conditions. We identified more than 50 oxygenated organic compounds in the gas and particle phases obtained from chamber oxidation of 13BD. Some reaction products have been reported in the literature, but several others were identified for the first time: glyceric acid-organosulfate, 2(3*H*)-furanone, dihydro-3,4-dihydroxy-organosulfate (2 isomers), threonic acid-organosulfate, 1,2,3,4-butanetetrol nitrosoxy-organosulfate, 1,2,3,4-butanetetrol nitroxy-organosulfate, malic acid-organosulfate, and threonic acid nitroxy-organosulfate. The quantitative analysis showed that glyceric acid, threitol, erythritol, threonic acid, several dimers, unknowns, and organosulfates were the most abundant components of 13BD SOA under acidified and non-acidified seed conditions. Other components contributing to SOA mass were diols, mono- and dicarboxylic acids, organosulfates, dimers, and nitroxy- and nitrosoxy-organosulfates. Several carboxylic acids, organosulfates and nitroxy-organosulfates identified in chamber samples were also detected in ambient aerosol samples collected at various sites in Poland. Such consistency reinforces the relevance of the chamber findings even though some components were found only in chamber experiments.

Comparison between experiments conducted with acidified and non-acidified seed aerosol at various RH revealed that acidity of seed aerosol (ER444), aerosol phase state (ER444 vs. ER666), and RH (ER444 and ER666) influenced the production of SOA as well as the number and molecular structure of products formed in the gas and particle phases. Total SOC decreased with increasing RH, but the levels of individual components varied, though the majority followed similar trends as the SOC. Ozone production and conversion efficiency of 13BD depended on RH, aerosol phase state, and acidity of the seed aerosol similar to SOC. The concentrations of most compounds decreased as RH increased, but few products were most abundant at intermediate RH around 30% (e.g., malic acid, glyceric acid-OS). This is also true for gas phase formaldehyde and acrolein, whose yields increased significantly at higher RH. However, at high humidity, the difference was relatively small. For the range of RH considered, the acidified seed experiments, in which the aerosol particles were deliquescent, enhanced SOC production compared to non-acidified seed experiments, in which the aerosol particles did not contain aqueous phase. SOC production increased with the acidity of the aqueous phase in the acidified seed experiment ER444. Yields of the individual SOA components followed the same pattern as SOC, while a few were more abundant in non-acidified seed experiments (e.g., unknowns) or behaved in an inconsistent manner. Although, the terms “acidified” and “non-acidified” is true for the solutions from which the seeds were atomized, there is far more fundamental differences between the phase states in which species partition to or from (aqueous/solid), which considerably affects their partitioning and formation mechanisms. Therefore, further research is needed to elucidate the mechanisms of their formation and partitioning in the atmosphere, both for dry and deliquescent particles. Overall, the 13BD results are consistent with those reported by Nestorowicz et al. (2018) for isoprene.

The present study employed analytical methods suitable for a wide range of 13BD reaction products in the particle and gas phases at various RH and seed aerosol acidity. It provided a solid identification of wide variety of reaction products including HAPs, dimers and organosulfates, as well as quantitative changes in their formation as a function of RH and seed aerosol acidity. Certainly, this study includes some uncertainties that need to be addressed in future work. Perhaps the most significant improvement would be the use of authentic standards to better quantify the contribution of individual products to SOA at various RH and seed aerosol acidity. This study shows that SOA and SOC consistently increased with decreasing RH and were higher under acidified than non-acidified seed conditions. Similar trends were observed for the majority of reaction products reported in this study. To assess that observation, the LWC and other thermodynamic properties of the aerosol phase were estimated as a function of RH using the thermodynamic model E-AIM. Organic acids could have more profound influence, especially for the non-acidified seed experiment, so the results of our modeling should be taken as a first approximation and verified as soon as the precise stoichiometry of the acids formation and reliable dissociation constants of those acids are available.

13BD does not contribute more to atmospheric aerosol than isoprene, which is emitted to the atmosphere in a much larger amount and plays a significant role in atmospheric SOA modelling. However, 13BD emissions are less understood than isoprene, and current increases in wildfires and

areages burned due to climate issues can increase 13BD emissions and therefore the production of 13BD SOA, which may have implications for air quality, health, and well-being.”

We replaced the word “acidic” by “acidified” throughout the manuscript and SI including figures and Tables to reflect the editor concerns. We also make sure that the term “acidified” and “non-acidified” is associated with the seed aerosol solution.

The title was changed from:

“Atmospheric oxidation of 1,3-butadiene: influence acidity and relative humidity on SOA composition and hazardous air pollutants”

To

“Atmospheric oxidation of 1,3-butadiene: influence of seed aerosol acidity and relative humidity on SOA composition and the production of air toxic compounds”

3. If experiments were performed that isolated the effects of acidity without an accompanying change in phase state, such conclusions could be drawn, but without that, the effects of acidity are not separable from those of phase state.

Authors reply:

We completely agree with the editor on this comment. However, our experiment ER444 presents a series of stages at changing RH (therefore changing acidity due to dilution) but without a change in phase state (all stages in ER444 have deliquescent particles). ER444 shows that in most cases acidity promoted formation of the products. To reflect the editor concern and make sure that this statement is exclusively associated with experiment ER444, we changed the following paragraph (page 31, lines 17: re-revised manuscript) from:

“The yield trends observed in acidic experiments, in which the aqueous particle phase was always present, may indicate that acidity enhances the formation of most products of 13BD oxidation in the aqueous phase. The concentration trends observed in non-acidic experiments, in which the particles contained no aqueous phase, may indicate that gaseous H₂O limited access of reactants to particle surfaces and hindered the formation of most products. A few exceptions to the major yield trend may indicate more complex formation mechanisms involved, which cannot be explained based on current work.”

To

“The yield trends observed in acidified seed experiments (ER444), in which the aqueous particle phase was always present, indicate that acidity enhances the formation of most products of 13BD oxidation in the aqueous phase. The concentration trends observed in non-acidified seed experiments (ER666), in which the particles contained no aqueous phase, may indicate that the phase state and/or gaseous H₂O limited access of reactants to particle surfaces and hindered the formation of most products. A few exceptions to the major yield trend may indicate more complex formation and partitioning mechanisms involved, which cannot be explained based on current work. In addition, the “acidified” and “non-acidified” terms are associated with seed aerosol solutions, and fundamental differences in chemical mechanism may be responsible for the reaction products formed in this study due the phase states in which the particles themselves exist, liquid (ER444) or solid (ER666).”

To reflect the Editor’s concern, we also changed the following sentences (page 31 line 5: re-revised manuscript) from:

“The concentration of the majority of reaction products (1) was higher under acidic conditions, than under non-acidic conditions, across the RH used in this study, (2) decreased with increasing RH either under acidic or non-acidic conditions (Figures 12, 13, 14, 17, and S13 – S43). “

To

“The concentration of the majority of reaction products (1) was higher under acidified seed aerosol conditions, where the aerosol particles contained aqueous phase, than under non-acidified seed conditions, where the aerosol particles did not contain any aqueous phase, across the RH range used in this study, (2) increased with the acidity of the aerosol aqueous phase in the experiments under acidified seed conditions, with aqueous phase always present; and (3) decreased with increasing RH either under acidified or non-acidified seed conditions (Figures 12, 13, 14, 17, and S13 – S43).”

4. The authors pointed out in their response to reviews that particle phase state was discussed in the original manuscript. However, the fact that both reviewers remained troubled by the interpretations, and that the manuscript's data interpretation point conclusively to the effects of acidity despite not separating the confounding effects of phase state, means that the original discussion of phase state in the paper was insufficient. I'd therefore like to ask that the authors further revise the manuscript to clarify, throughout, that the observed differences *may* be due to acidity, but alternatively *may* be due to phase state or liquid water content, and remove the statements that directly attribute observed differences to particle acidity. The abstract and summary (and ideally title) should only provide conclusive statements about what can be directly supported by the data, which does not include effects of particle acidity alone. Further discussion about the potential role of phase state alone would also help; the added paragraph at the end of Section 3.2.3 is useful for this purpose, but remains

vague and unsupported by evidence (how do we know that the LWC equilibration time is "probably" on the order of minutes? Citations here would help).

Authors reply:

We thank the Editor for pointing this out. We feel that our response to the previous comments (see above) by the Editor highlights clearly the comments raised by the Editor here. We further added the following sentences to page 31, line 25 and reads:

“The observed differences between the acidified (ER444) and non-acidified (ER666) seed aerosol experiments may be due to the acidity of the seed aerosol, liquid water content, and/or the phase state of the aerosol particles. Furthermore, more work is needed to gain insight into mechanisms of reactant formation and partitioning to deliquescent particles and to particles lacking the aqueous phase.”

We prepared the acidic and non-acidic seed aerosol with the method that has been used in chamber experiments for decades. In our new revised manuscript, we feel strongly that our new terminology “acidified seed aerosol” and “non-acidified seed aerosol” reflects the experimental conditions used in this study. We apologies for any misunderstanding associated with the terms “acidic” and “non-acidic”.

To reflect the editor concerns, we replaced the last paragraph in section 3.2.3 that reads:

"As stated above, the non-acidic seed aerosols were dry based on E-AIM modelling. This may be a major difference in the acidic and non-acidic conditions and probably one of the main drivers of differences in the chemistry between the two systems. Note that E-AIM is an equilibrium model, which has its own limitations. Therefore, it is important to consider that under our experimental conditions, the system should be at chemical equilibrium, which can be difficult to characterize. In our experimental system, we are going from liquid solution in the nebulizer reservoir, to ammonium sulfate particles in near -100% RH air exiting the nebulizer to chamber dry air in less than a minute. Then the particles have a chance to equilibrate in the chamber for a matter of hours. The equilibrium time needed for acidic wet aerosols to adjust their LWC to the chamber RH conditions is probably on the order of minutes, so they are probably close to their E-AIM predicted LWCs in the chamber. However, the time needed for the wet neutral aerosols to completely dry out at room temperature may be on the order of hours. It is probable that under our experimental conditions the wet neutral aerosol do not reach the E-AIM predicted dryness on the time scale of the chamber residence time. This may explain why the two systems are not drastically different chemically as expected.”

With the following paragraph (last paragraph in section 3.2.3 in the re-revised manuscript and reads:

“The preparation of non-acidified and acidified seed aerosol by nebulizing aqueous solutions of NH_4SO_4 and $(\text{NH}_4\text{SO}_4 + \text{H}_2\text{SO}_4)$, respectively, has been used in chamber experiments for many years

(Czoschke et al., 2003; Deng et al., 2021; Zhang et al., 2023). As stated above, the LWC and acidity of the aerosol were estimated using E-AIM modeling, which assumes the vapor-particle partitioning equilibrium in the system. The non-acidified seed aerosols were dry based on E-AIM modelling. This may be a major difference in the acidified and non-acidified conditions and probably one of the main drivers of differences in the chemistry between the two systems. Note that E-AIM is an equilibrium model, which has its own limitations. Therefore, it is important to consider that under our experimental conditions, the system should be at chemical equilibrium, which can be difficult to characterize. In our experimental system, we are going from liquid solution in the nebulizer reservoir, to ammonium sulfate particles in near -100% RH air exiting the nebulizer to chamber dry air in less than a minute. Then the particles have a chance to equilibrate in the chamber for a matter of hours. The equilibrium time needed for acidified wet aerosols to adjust their LWC to the chamber RH conditions is probably on the order of minutes to ten of minutes (Saleh et al. 2013), so they are probably close to their E-AIM predicted LWCs in the chamber. However, the time needed for the wet neutral aerosols to completely dry out at room temperature may be on the order of hours. It is probable that under our experimental conditions the wet neutral aerosol do not reach the E-AIM predicted dryness on the time scale of the chamber residence time. This may explain why the two systems are not drastically different chemically as expected.”

The following reference were added to the re-revised manuscript.

Czoschke, N. M., Jang, M., and Kamens, R. M.: Effect of acidic seed on biogenic secondary organic aerosol growth, *Atmos Environ*, 37, 4287-4299, [http://dx.doi.org/10.1016/S1352-2310\(03\)00511-9](http://dx.doi.org/10.1016/S1352-2310(03)00511-9), 2003.

Deng, Y., Inomata, S., Sato, K., Ramasamy, S., Morino, Y., Enami, S., and Tanimoto, H.: Temperature and acidity dependence of secondary organic aerosol formation from α -pinene ozonolysis with a compact chamber system, *Atmos Chem Phys*, 21, 5983-6003, <https://doi.org/10.5194/acp-21-5983-2021>, 2021.

Saleh, R., Donahue, N. M., and Robinson, A. L.: Time Scales for Gas-Particle Partitioning Equilibration of Secondary Organic Aerosol Formed from Alpha-Pinene Ozonolysis, *Environmental Science & Technology*, 47, 5588-5594, <https://doi.org/10.1021/es400078d>, 2013.

Zhang, J., Shrivastava, M., Zelenyuk, A., Zaveri, R. A., Surratt, J. D., Riva, M., Bell, D., and Glasius, M.: Observationally Constrained Modeling of the Reactive Uptake of Isoprene-Derived Epoxydiols under Elevated Relative Humidity and Varying Acidity of Seed Aerosol Conditions, *ACS Earth and Space Chemistry*, 7, 788-799, <https://doi.org/10.1021/es400078d>, 2023.

5. (If, as the authors suggest in one reviewer response, this is all just a misunderstanding because "acidic" vs. "non-acidic" refers to the initial atomizer solution and not the particles, that needs to be very well clarified throughout. The authors should then use different descriptors to separate the two experiments, because the current terminology is misleading, as it strongly implies that particle acidity (not atomizer solution acidity) is the factor on which subsequent organic aerosol composition differences depend).

Authors reply:

This comment is clearly clarified in the re-revised manuscript (see our response to the previous comments of the Editor above).

6. Like the reviewers, I believe this manuscript will be a valuable addition to the literature once it is revised such that its conclusions are better supported by the evidence provided throughout, and I hope the authors agree that this will improve the manuscript's clarity and usefulness. I look forward to reading a new revision.

Authors reply:

We greatly appreciate the Editor for his valuable input and comments. We feel that the conclusions in the re-revised manuscript are supported by the evidence provided throughout the manuscript.