

RC2 review

In “Atmospheric oxidation of 1,3-butadiene: influence of acidity and relative humidity on SOA composition and air toxic compounds,” Jaoui et al. analyzed the composition of SOA prepared from 1,3-butadiene in the presence of NO_x under varying acidity and humidity levels, including both the gas and particle phases. They found increased production of SOC at elevated RH and increased acidity, although some individual compounds varied from these trends. They also identified and reported several compounds from the oxidation of 1,3-butadiene for the first time. The analysis presented was in-depth and informative, and worthy of publication after the following points are addressed.

Authors' reply:

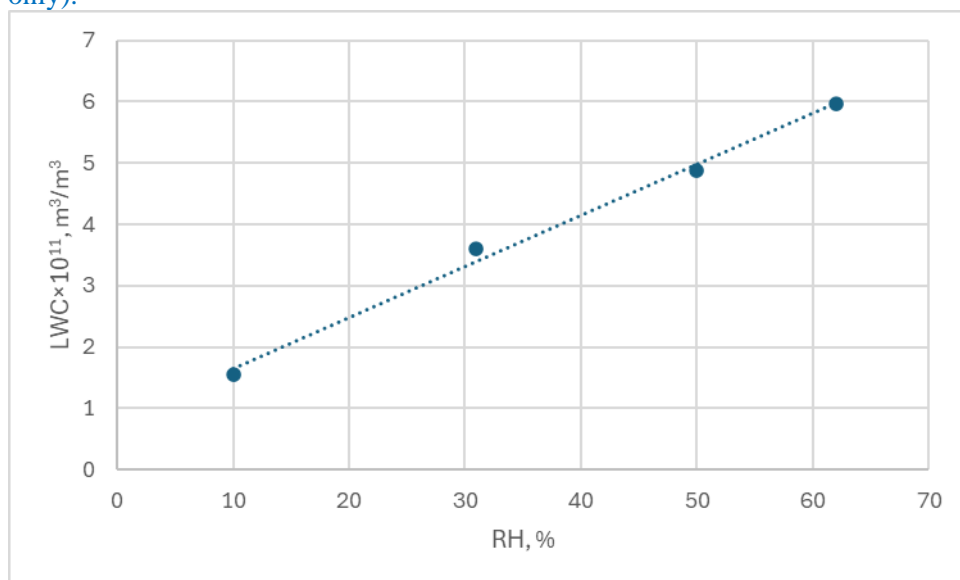
We thank the Reviewer for the effort to evaluate our manuscript and for the positive opinion on it.

Major Feedback

1. The stated goals of the paper are not the major points of discussion throughout the work. For example, the authors state the purpose of the paper is to analyze the impacts of LWC on SOA formation, but LWC is not discussed in the paper other than Page 29 line 7 where it is related to acidity. I think LWC warrants more discussion, particularly for the non-acidified seed particle experiments where some of the seed particles are likely effloresced. I would expect a large difference in chemical behavior between solid and aqueous particles.

Authors' reply:

LWC estimated using the E-AIM model was zero in all non-acidic experiments as written in the original manuscript (p. 29 line 24), so it could not influence the results. In the acidic experiments, LWC increased proportionally with RH (Table 6 in the original manuscript and the plot below), so the influence of LWC is equivalent to that of RH (in the acidic experiments only).



We provided additional discussion in our response to reviewer #1 to his general comments. (please refer to that comment for additional info).

2. Many of the identified products appear to be OH oxidation products judging by retention of the 4-carbon backbone. Do the authors have an estimate of the steady state OH concentration? Does it change with any of the parameters they are varying (perhaps with LWC)? Given the importance of OH oxidation in the atmosphere, and that it is the major atmospheric sink for isoprene, the impact of the variables on OH concentrations should be considered.

Authors reply:

The reviewer makes a good point. This is correct that OH radicals are the main oxidant in our system both under acidic and non-acidic conditions. Unfortunately, we don't have the capability in our lab to measure OH radicals in the gas phase.

We provided additional discussion concerning this comment in our response to reviewer #1 (section Discussion; comment #1). In that response we added the following sentences to the manuscript (please refer to that comment for additional info).

“It has been reported that RH changes promote changes in OH radical concentrations (Hu et al., 2011). These changes may be one of the reasons for the RH affecting the photochemical conversion of 13BD in our study.”

3. If possible, the section on field measurements should be strengthened. The results would be more meaningful if 13BD had also been measured at the sites, but from my understanding there were only particle measurements taken in the field. It is stated in the intro that 13BD is mostly from anthropogenic sources, and then it is stated that the site in Godow has more anthropogenic influence than the other sites. Were the 13BD products higher there than in the other sites, or is there other evidence that the concentrations of proposed 13BD oxidation products are higher in areas where higher levels of 13BD are expected to be found?

Authors' reply:

In our field campaigns, we collected the ambient aerosol samples only and relied on the routine measurements from the monitoring stations at which we sampled. Unfortunately, 13BD is not routinely measured at Polish monitoring stations. However, the purpose of presenting the field results was to show that compounds determined in smog-chamber experiments occur also in the real ambient aerosol. The quantitative analysis of those compounds in the atmosphere at specific locations was far beyond the scope of our work.

To reflect the reviewer concern, we added the following sentence to the revised manuscript on page 32, line 2 and reads:

“The purpose of presenting the field results was to show that some compounds observed in smog-chamber experiments occur also in the real ambient aerosol.”

Minor Feedback

Page 3 Line 25-30 - This statement could be clarified or perhaps made more specific. What is meant by “bulk properties” versus “composition?” Several of the listed citations for only “bulk properties” show analysis of composition. I think perhaps the authors are trying to differentiate between studies that looked at only particle composition versus studies that also included the gas phase composition. There have been several further studies on the effects of RH on particle composition since 2021.

For example:

<https://doi.org/10.1039/D3EA00033H> Klodt

<https://doi.org/10.1039/D3EA00149K> Luo

<https://doi.org/10.1039/D3EA00128H> Thomsen

There are likely others that I did not find in my brief search, and the earlier studies in this collection of work may be better represented by a review paper if one is available. Also, the year for the Hinks reference should be 2018, rather than 1918.

Authors' reply:

We refer to SOA “bulk properties” those properties that are associated with macro-parameters of the aerosol such as yield, SOC, SOA of the aerosol.

We added references to the revised manuscript as suggested by the reviewer. See also specific comment #1 from reviewer # 1, specific comments)

1. Klodt, A. L., Aiona, P. K., MacMillan, A. C., Lee, H. J., Zhang, X., Helgestad, T., Novak, G. A., Lin, P., Laskin, J., Laskin, A., Bertram, T. H., Cappa, C. D., and Nizkorodov, S. A.: Environ. Sci.: Atmos., Effect of relative humidity, NO_x, and ammonia on the physical properties of naphthalene secondary organic aerosols, 3, 991, doi.org/10.1039/D3EA00033H, 2023.
2. Luo, H., Guo, Y., Shen, H., Huang, D. D., Zhangabcef, Y., and Zhao, D.: Effect of relative humidity on the molecular composition of secondary organic aerosols from a-pinene ozonolysis, Environ. Sci.: Atmos., 4, 519, doi.org/10.1039/D3EA00149K, 2024.
3. Thomsen, D., Iversen, E. M., Skønager, J. T., Luo, Y., Li, L., Roldin, P., Priestley, M., Pedersen, H. B., Hallquist, M., Ehn, M., Bilde, M., and Glasius, M.: The effect of temperature and relative humidity on secondary organic aerosol formation from ozonolysis of D₃-carene, Environ. Sci.: Atmos., 4, 88, doi.org/10.1039/D3EA00128H, 2024.

Page 5 line 2 - Does all of the radiation fall between 300 and 400 nm? It could be useful to provide a graphical comparison between the lamp spectrum and the solar spectrum in the SI, unless it is provided in one of the references.

Authors' reply:

As stated in our manuscript (page 5, lines 1, 2), the UV fluorescent bulbs used in the chamber produce radiation in the actinic region of the spectrum at 300-400 nm photolytically comparable to that of solar radiation (Black et al., 1998). The readers should consult Black et al., 1998 paper.

Page 5 line 6 - What was the approximate pH of the non-acidified seed aerosol? I would expect it to be between 4 and 5, so “non-acidified” would be a more accurate description of the seeds than “non-acidic” The EAIM results for the non-acidified conditions should also be included in the paper. As the dissolved organic acids will have a significant effect on the pH for the unacidified conditions, the

authors could also consider adding some concentration of a representative organic acid to the calculations to get a general idea of the pH of the particles during these experiments.

Authors' reply:

The results of E-AIM modeling of non-acidic seed experiments have been included in the original manuscript (p. 29, lines 24-25; input data in Supplementary, p. 19) – there was no aqueous phase in all non-acidic experiments. The influence of dissolved organic acids produced from 13BD was not considered as explained in the original manuscript (p. 29, lines 28-34). It could be marginal in acidic-seed experiments due to dominating inorganic acidity. It could be more profound in non-acidic experiments, but we were not able to evaluate it quantitatively because of lacking stoichiometric and dissociation data.

We believe the reviewer refers mainly to the terminology. Acidified aerosol means a laboratory prepared acidic seed aerosol introduced into the chamber initially and the actual pH of the wet seed without added acidification from acids present in the aerosol phase. For example, if one adds the wet aerosol from the nebulizer to the chamber at an RH greater than the efflorescence RH (ERH) of ammonium sulfate (ca. 30%), the seed aerosol will stay at a liquid state. This is the condition the reviewer is referring to. If non-acidified aerosol is introduced to the chamber with an $RH < 30\%$, then the aerosol will not retain its wetness.

Table 1 - What is the significance of the experiment set names? I found them difficult to remember on initial read through. Since they are currently separated by acidity level, could they be referred to using an abbreviation that correlates to their acidity level?

Authors' reply:

We thank the reviewer of this comment. We chose to keep these names for quality controls purpose. These names are associated with the original experiment's names.

Page 10 Line 6 - Are the authors referring to wall loss here? Or is there another type of loss they anticipate?

Authors' reply:

We thank the reviewer for this comment. Yes, we refer to wall loss here. We changed the following sentence (page 10, line 6) from:

“Given the experiments were conducted in flow mode, we anticipate the loss in particle and gas phase products including 13BD to be negligible as the measurements were conducted at steady state conditions.”

To

“The wall loss of particles is ~6% per hour. We expect gas phase products and 13BD wall to be negligible as the experiments were conducted at steady state conditions, and in flow mode.”

Table 4 – It would be informative if the authors could provide a ratio of intensity in acidified to unacidified conditions (or vice versa). They would then have the option to comment on the relative production of the compound under each condition.

Authors' reply:

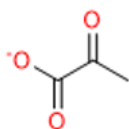
We are not certain what the reviewer is referring to here as “intensity.” Is this a reference to GC signal intensities (or estimated concentrations)? If so, this ratio would provide a good indication of the differences in abundance of the identified compounds under the different conditions tested. However, this would not be straightforward to do, because we have multiple RH conditions as an additional dimension in these measurements, which would make a simple ratio unworkable, or at least much more complex than a single ratio per compound.

Figure 6 - The authors show the less acidic carboxylic acid being deprotonated for oxaloacetic acid. This structure would make the decarboxylation they show less favorable. The fragmentation pathway for this intermediate has been presented before in acidified and unacidified ammonium sulfate solutions under conditions relevant to this work: <https://doi.org/10.1021/acsearthspacechem.1c00025>

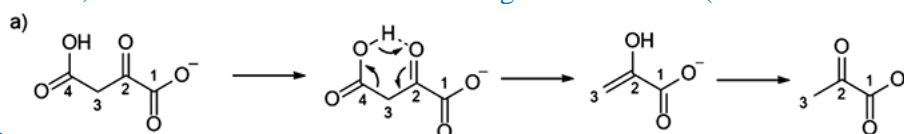
Authors' reply:

If we understand the reviewer's comment correctly, that one of the two structures we proposed for the m/z 87 ion, i.e., the product ion from the decarboxylation of deprotonated oxaloacetic acid precursor ion (m/z 131) is less favorable. In Figure 6 we proposed the two possible structures for m/z 87 ion:

First:

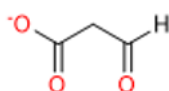


which is consistent with the Klods' paper – stating that the decarboxylation proceeds through the proposed scheme, which include a six-membered ring transition state (see Scheme 2 in the



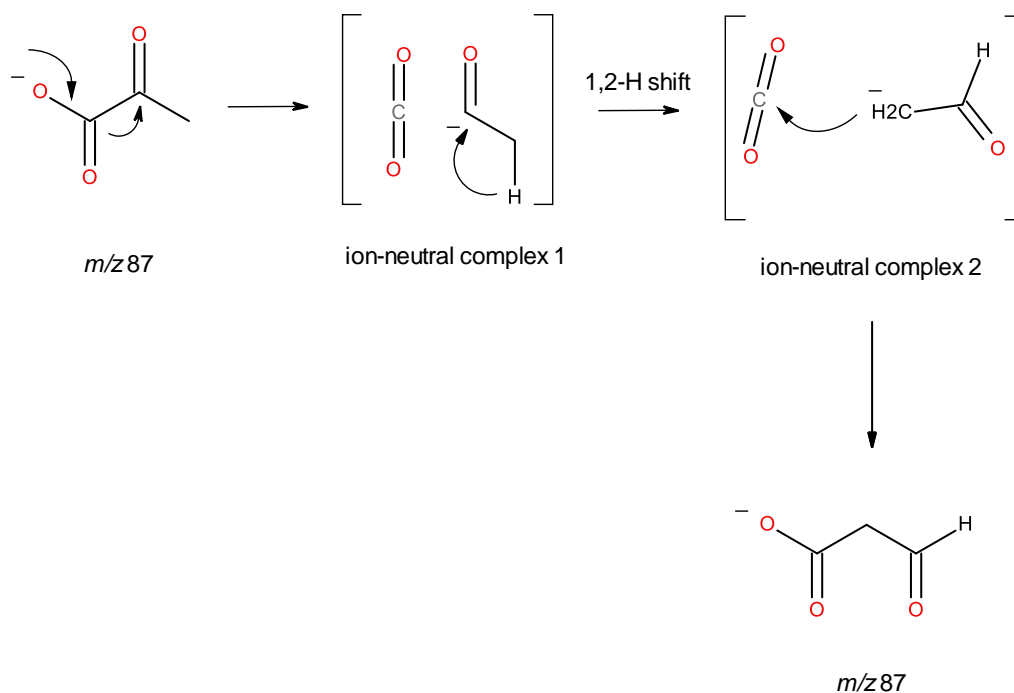
Klod's paper):

However, the second structure we proposed is also possible:



In contrast to solution chemistry, our results presented in Scheme 6 refer to fragmentation reactions in the negative electrospray mass spectrometry. These gas-phase reactions cover not only simple C-C bond breaking, which are typical of solution chemistry but also rearrangements, where two bonds may decompose simultaneously giving rise to an isobaric product. The reviewer states that the second proposed structure is “less favorable”. However,

the formation of latter could be easily explained through the ion-neutral complex-mediated reactions, which are recognized mechanisms in mass spectrometry (Longevialle, *Mass Spectrom Rev.*, 1992, 11, 157-192). As shown below, the m/z 87 ion may decompose through the negative charge-initiated fission of the adjoined C-C bond resulting in the formation of a short living ion neutral complex 1. While travelling to the detector, such a complex may decompose leading to m/z 43 product ions (not observed in our mass spectra in Figure 6) but also the 1,2-H shift reaction may occur between the neutral molecule (CO_2) and a charged fragment of the complex, which leads to a novel ion-neutral complex 2. Once it is formed, the carboxylation happens leading to isobaric structure of the m/z 87 ion that we postulated in Figure 6:



References

Alexandra L. Klodt; Kimberly Zhang; Michael W. Olsen; Jorge L. Fernandez; Filipp Furche; and Sergey A. Nizkorodov. Effect of Ammonium Salts on the Decarboxylation of Oxaloacetic Acid in Atmospheric Particles. *ACS Earth Space Chem.* 2021, 5, 4, 931–940.

Longevialle, Pierre. Ion–neutral complexes in the unimolecular reactivity of organic cations in the gas phase. *Mass Spectrom Rev.*, 1992, 11, 157-192.

Page 32 lines 18 through 20 - When the authors say the compounds they identified in this work were not found in SOA from other precursors, do they mean just the ones identified in Tables 4 and 5, or just the 4 compounds listed earlier in the section? Because several of the compounds mentioned in the paper, for example formaldehyde, should be common oxidation and photolysis products.

Authors' reply:

We thank the reviewer for this comment. To reflect his concern, we changed the following sentence (page 32) from

“Note that samples from chamber experiments conducted in our laboratory involving the oxidation of biogenic (e.g., isoprene, monoterpenes, sesquiterpenes, 2-methyl-3-buten-2-ol), aromatic (e.g., toluene, 1,3,5-trimethylbenzene, benzene), and polycyclic aromatic hydrocarbons (PAHs) (e.g., naphthalene) did not contain the compounds identified in work using the same experimental and analytical procedures.”

To

” Note that samples from chamber experiments conducted in our laboratory involving the oxidation of biogenic (e.g., isoprene, monoterpenes, sesquiterpenes, 2-methyl-3-buten-2-ol), aromatic (e.g., toluene, 1,3,5-trimethylbenzene, benzene), and polycyclic aromatic hydrocarbons (PAHs) (e.g., naphthalene) did not contain the compounds identified in this section except malic acid and tartaric acid using the same experimental and analytical procedures.”