

RC1 review

This is the review for manuscript entitled “Atmospheric oxidation of 1,3-butadiene: influence of acidity and relative humidity on SOA composition and air toxic compounds” by Jaoui et al.

This study investigates the effect of RH on the chemical composition of both gas and particle phases formed from the photooxidation of 1,3-butadiene (13BD) under acidic and non-acidic conditions. The authors identified a variety of products formed through the reaction. They find SOA mass and the most SOA products under acidic and lower RH conditions. With increased RH, secondary organic carbon decreased under acid and non-acid conditions. The authors state that the photochemical reactivity of 13BD in our systems decreased with increasing RH and was faster under non-acidic than acidic conditions. Overall, the results from this study present potential to improve the current understanding of atmospherically relevant aerosol particles. The manuscript is clearly written, and I enjoyed reading it. I mostly suggest minor revisions and clarifications, though a major revision might be needed address an alternative interpretation of the influence of acidity and RH.

Authors' reply:

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

General Comments:

The manuscript discusses the impacts of RH and acidity affects oxidation reactions and products. The changes in RH will modify the acidity of aerosols. It remains unclear how the authors determine the relative influence of those factors. Authors need to clarify their approach in differentiating and quantifying the impact of RH and acidity on SOA formation.

Authors' reply:

The Reviewer is correct. RH and acidity of aerosols are related for a given aerosol composition. Note though, our experiments were conducted under two conditions: (1) in the absence of acidic seed aerosol (ER666, Table 1) and only the RH was changed from 11 to 60%; (2) under acidic seed aerosol (ER444, Table 1), and then only the RH was changed from 10 to 62%. Then the relative influence of RH can be assessed from both experiments ER444 (under acidic conditions) and ER666 (under non-acidic conditions) as only RH was changed. Although, small acidity changes may occur with changes in relative humidity as indicated by the reviewer, which is happening under acidic and non-acidic conditions (ER444 and ER666), but it is part of the effect of RH also. However, it is difficult to characterize the changes in SOA reaction products, which may be due to dilution, and/or chemical reactions occurring either in the gas or particle phase or both. The effect of RH was discussed in section 3.2.1. The effect of acidity at the same RH was reported in section 3.2.2.

In addition, to assess that relation in all our experiments, we used the widely used Extended-AIM Thermodynamic Model (E-AIM) as explained in the manuscript, section 2.5 p. 8 lines 15-24. The input data for the model are RH, temperature, and quantitative aerosol composition (Section S2 in the Supplementary).

The aqueous aerosol phase occurred only in all acidic-seed experiments, where “*The acidity of the aqueous phase decreased, and LWC increased with increasing RH. The pH (aH^+) of the aqueous phase increased from -1.79 at 10% RH to ~0.40 at 62% RH*” as we have written in

the original manuscript (Section 3.2.3, p. 29, lines 27-28). Thus, we feel that the comment has already been addressed in the original manuscript.

The study explores a range of RH from 11-60%. At 11% RH, ammonium sulfate particles are likely in the solid phase, which may involve different chemical mechanisms compare to those in the aqueous phase. Authors should consider how the phase states affect aerosol chemistry and the products observed.

Authors' reply:

Again, this is an important point raised by the reviewer. E-AIM modeling showed that the aqueous aerosol phase was absent across all RH conditions in non-acidic seed experiments (Section 3.2.3, p.29, lines 24-25). On the other hand, aqueous aerosol phase occurred in all acidic seed experiments (Section 3.2.3, p. 29, Table 6). Thus, the results of the non-acidic seed experiment refer to non-aqueous chemistry. In contrast, the acidic-seed experiments include the influence of the aqueous-phase chemistry and the acidity of the aqueous aerosol phase. We addressed that difference in the original manuscript (p. 30 lines 16-20): "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." Thus, we believe that this comment has been addressed in the original manuscript.

As stated above, based on the E-AIM modelling the non-acidic aerosols were dry. 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. It is important to note that E-AIM is an equilibrium model, which has its own limitations, and it is out of the scope of this paper. Therefore it is important to note that under our experimental conditions, the system should be at chemical equilibrium, which is 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.

To reflect the reviewer concern, we added the following paragraph to the manuscript at the end of section 3.2.3, where E-AIM was discussed.

"As stated above, the non-acidic 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 is 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 aerosols 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.”

This study did not include the toxicity of compounds formed from SOA; the author may modify the title of the paper to be more relevant.

Authors' reply:

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

Specific Comments :

Introduction

1. The literature citations need to be updated. Several recent studies indicating how acidity influences SOA formation should be included:

- Decreases in Epoxide-Driven Secondary Organic Aerosol Production under Highly Acidic Conditions: The Importance of Acid–Base Equilibria Madeline E. Cooke, N. Cazimir Armstrong, Alison M. Fankhauser, Yuzhi Chen, Ziyang Lei, Yue Zhang, Isabel R. Ledsky, Barbara J. Turpin, Zhenfa Zhang, Avram Gold, V. Faye McNeill, Jason D. Surratt, and Andrew P. Ault *Environmental Science & Technology* 2024 58 (24), 10675-10684 DOI: 10.1021/acs.est.3c10851
- Initial pH Governs Secondary Organic Aerosol Phase State and Morphology after Uptake of Isoprene Epoxydiols (IEPOX) Ziyang Lei, Yuzhi Chen, Yue Zhang, Madeline E. Cooke, Isabel R. Ledsky, N. Cazimir Armstrong, Nicole E. Olson, Zhenfa Zhang, Avram Gold, Jason D. Surratt, and Andrew P. Ault *Environmental Science & Technology* 2022 56 (15), 10596-10607 DOI: 10.1021/acs.est.2c01579

Authors' reply:

The references are now incorporated on page 3, line 23 The references were added to the reference section.

Method

1. The manuscript should address the wall loss of particles within the smog chamber. what is the residence time of particles in the smog chamber?

Authors' reply:

For a wide range of particles, the wall loss rate is 0.063 h^{-1} .

We added the following sentences on page 5, line 28 (original manuscript).

“For a wide range of particles, the wall loss rate is 0.063 h^{-1} . However, with the chamber running in a flow mode the wall loss rate is subsumed in the observed decrease from the input reactants and the steady-state concentrations.”

The residence time of 4 hour was reported in the manuscript in section 2.1.

2. The manuscript does not mention the concentration of ammonium sulfate and sulfuric acid solutions under acidic and non-acidic conditions.

Authors' reply:

We have included that information in the Supplementary (Section S2. p. 19).

3. It is unclear whether each experiment started at the lowest RH, approximately 11%. If so, the ammonium sulfate seed particles would be below the efflorescence point and remain in the solid phase across the RH range, influencing SOA formation differently compared to reactions in the liquid phase. Can the authors confirm and discuss this?

Authors' reply:

We showed by E-AIM modeling that in all non-acidic seed experiments (RH = 11-60%) there was no aqueous phase while in all acidic-seed experiments (RH = 10 – 62%) the aqueous phase occurred. As noted above, the results of non-acidic seed experiment refer to non-aqueous chemistry while the acidic-seed experiments include the influence of the aqueous-phase chemistry and the acidity of the aqueous aerosol phase (original manuscript, p. 30 lines 16-20). Please refer to our response to your general comments.

4. Changes in RH also affect aerosol acidity. How do the authors assess the impact of pH changes along with RH adjustments? Furthermore, aerosol size significantly affects aerosol pH. Were the inorganic seed particles size-selected before being introduced into the smog chamber? An explanation on how size effects on aerosol acidity were ruled out would be beneficial.

Authors' reply:

We addressed the relation of RH and aerosol acidity in the previous parts of our response. The influence of aerosol size on aerosol acidity generally refers to atmospheric aerosols and is controlled by chemical composition, variation of inorganic aerosol composition with size, hygroscopicity, and timescale differences of gas-particle equilibration (mass transfer). The seed aerosol in smog-chamber experiments is prepared and has a defined chemical composition so its acidity does not depend on particle size. Formation and partitioning of reaction products, especially organic acids, to seed-aerosol particles could affect the aerosol acidity, but we neglected that influence because we did not know the exact stoichiometry of dissociable hydrogen ions production during their formation as well as reliable dissociation constants. We reported that in the original manuscript (p.8, Section 2.5, lines 21-23).

While we appreciate the reviewer's comments, the effect of particle size on the results was not studied and this consideration is out of the scope of this study.

5. How many experiments were conducted under the various conditions, and how repeatable are the results?

Authors' reply:

We have conducted more than 10 experiments of this particular experimental design, and the experiments are reproducible within the experiment's uncertainties. Though it is impossible to repeat experiments exactly, good reproducibility has been achieved vis-a-vis the aerosol yield and the compounds observed. Repeatability of RH conditions was quite good. Repeatability of seed aerosol conditions was more challenging, which was why these experiments involved changing the RH while the seed was kept constant rather than holding the RH constant and changing the seed.

6. The RH at the ambient sampling sites is consistently higher than that in the chamber conditions. Why were higher RH experiments not performed in this study?

Authors' reply:

For the steady-state operating mode used for these experiments, the highest stable RH level we could achieve was ~65% RH.

The primary purpose of presenting the composition of ambient samples was to show that some compounds observed in the chamber also occurred in the ambient aerosol. We did not attempt to compare the real and chamber processes quantitatively.

Discussion

1. Can the authors explain why the photochemical conversion of 13BD decreases with an increase in RH? The conversion efficiency of 13BD is higher under non-acidic conditions compared to acidic conditions. As the RH increases and the acidity decreases, this should logically result in an increase in 13BD conversion efficiency. Could the authors discuss this observation?

Authors' reply:

We did provide explanation for "The photochemical reaction of 13BD in the presence of NO_x decreases with an increase in RH" on page 8, lines 40-41. However, to reflect the reviewer concern, we added the following sentences to page 8, line 47 and read:

"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."

We added the following reference to the reference section:

Hu, G., Xu, Y., and Jia, L.: Effects of relative humidity on the characterization of a photochemical smog chamber, *J. Environ. Sci.* 23, 2013–2018, 2011.

We added also the following sentence on pages 29-30 (lines 40 and 1, respectively):

“On the contrary, the 13BD conversion efficiency was higher under non-acidic conditions than acidic (Figure 1b), indicating increased non-reactive uptake of 13BD by non-acidic seeds which contained no aqueous phase.”

The reviewer states that as “RH increases and the acidity decreases, this should logically result in an increase in 13BD conversion efficiency”. We don’t have any experimental evidence of this statement (RH increases can lead to acidity decreases) as we did not measure experimentally and don’t have the capability in our lab to measure the pH of the aerosol. Although our data suggest acidic compounds decreased with increases RH (Figure 12: top panel), we do not have any evidence that increases of RH lead to decreases in aerosol acidity (dilution effect). There is probably others chemistry be involved (e.g. heterogenous chemistry), and it is out of the scope of this study.

2. It is interesting to observe the concentration of the majority of products decreased with increasing RH, can author explain why?

Authors’ reply:

We have suggested the possible explanation in the original manuscript (Section 3.2.3, p. 30, lines 16-20). In the acidic-seed experiments, the aerosol acidity decreased with increasing RH, so we suggested that acidity enhances the formation of most products in the aqueous-phase. In the non-acidic-seed experiments, we suggested that formation of gaseous H₂O limited the access of reactants to aerosol surfaces and hindered the formation of most products.

3. Authors should consider add E-AIM result for non-acidic particles at different RH conditions for comparison and further understand the effect of acidity on SOA formation.

Authors’ reply:

We have done E-AIM modeling for non-acidic seed aerosol and described the results in the original manuscript (Section 3.2.3, p. 29, lines 23-25). In all non-acidic seed experiments, there aerosol aqueous phase was absent.

4. Page 24, Line 22, Need to add unit after 45.1.

Authors’ reply:

We added the unit as suggested by the reviewer.

5. Authors found that the higher concentration of the majority of reaction products under acidic conditions; however, it is not clear that this result is due to the effect of acidity, RH, or the phase state of seed particles.

Authors' reply:

We discussed this in our response to the first comment in the general comments of this reviewer. As we discussed in our original paper (section 3.2.2), there is clear evidence that acidity affects reaction products formation. We believe that this comment is discussed in our paper (section 3.2.2). Please note that the concentrations are in mass units per cubic meter of air. We respectfully acknowledge that the present work cannot explain the chemistry involved in our experiments better and that further work is needed (original manuscript, p. 30, lines 19-20; p. 33, lines 31-33).