

Interactive comment on “Atmospheric oxidation of isoprene and 1,3-butadiene: influence of aerosol acidity and relative humidity on secondary organic aerosol” by M. Lewandowski et al.

Anonymous Referee #2

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General comments:

This manuscript contributes to the growing body of knowledge on the relationship between aerosol acidity, humidity, and secondary organic aerosol (SOA) yield. Chamber experiments have repeatedly shown that SOA yields from isoprene and other ubiquitous volatile organic compounds (VOCs) increase dramatically with increasing particle acidity, and to a lesser extent correlate negatively with humidity (and particle water content) as well. However, field measurements frequently show only a minor dependence of ambient SOA on particle acidity. Reconciling these observations, and accurately quantifying the relationships between particle acidity, humidity, and SOA yields, would

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vastly improve our understanding of SOA formation from VOCs and improve our ability to model ambient SOA levels. This manuscript provides valuable chamber data validating previous measurements of isoprene SOA's dependence on acidity and humidity, and extends the analysis to 1,3-butadiene, another prominent VOC. The results for isoprene agree remarkably well with previous experiments, and those for 1,3-butadiene provide new insight into the variability of SOA yield-particle acidity interactions. However, as both the authors and the short comment by A. Nenes note, the methods used in this manuscript to measure bulk $[H^+]$ content are difficult to translate into atmospherically relevant parameters, and further experimentation and/or modeling will be needed to understand the atmospheric implications of these results.

Specific comments:

1) A major point of concern in this manuscript, as identified by the authors and further detailed in the short comment by A. Nenes, is the measurement of $[H^+]$ and its relationship with particle acidity and relative humidity. While the method used provides a valid bulk measurement, it is not clear whether bulk $[H^+]$ is particularly atmospherically relevant when other factors (e.g. particle water content) can influence acidity. In light of these concerns, I would suggest that the authors find addition methods, such as calculating particle acidity with a thermodynamic model, for approaching this intractable issue. As A. Nenes describes, such models have been shown to give reasonable estimates of aerosol pH, and when used in conjunction with measured bulk $[H^+]$, these estimates will provide a clearer interpretation of acidity in the particle phase. Of particular concern, in light of the difficulty of measuring particle acidity, are experiments in which multiple factors influencing acidity change together, such as the relative humidity experiments detailed in this manuscript. For reasons discussed in the manuscript, it can be hard to know how much the change in SOC yield reflects variations in humidity directly, or indirectly by changes in particle acidity, which may be changing despite a constant $[H^+]$ due to differences in particle water content. Employing thermodynamic models to estimate particle pH would be particularly useful for these experiments. Ad-

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ditionally, considering the difficulty of separating the effects of humidity and acidity in these experiments, discussion of further controls would be beneficial in Section 3.3. For example, the authors mention temperature differences between experiments (L320); could these temperature differences also have an effect on SOC yields? Also, when the relative humidity was stepped up and down in these experiments, could hysteresis effects influence SOC yield, by which particles formed at one humidity and then brought to another humidity have different organic content than particles formed at the second humidity level (e.g. by irreversible particle-phase reactions)? A discussion of these temperature and hysteresis effects, and particularly any control experiments run to investigate these effects, would provide valuable insight into the many factors at play in these humidity experiments.

2) Some discussion is needed at the end of the manuscript about the atmospheric relevance and implications of the results. Do these experiments provide any insight into field observations, and their persistent disparities from chamber experiments regarding the dependence of SOC yield on particle acidity? What effects might these humidity and acidity dependencies have on particle SOC yields in atmospheric conditions where isoprene and 1,3-butadiene are found?

3) Minor clarification questions about methods and instrumentation:

L151 – In the discussion of measuring $[H^+]$, some detail on the subject of uncertainty (e.g. the error bars shown on Figures 1, 2, 3, and 5) would be useful. How are these errors estimated, and what factors are (and are not) included?

L165 – A similar treatment of uncertainty in the discussion of particle organic carbon measurements would be useful as well.

L214 – What is the $[SO_2]$ background?

L579 – I believe figure 4 should have error bars similar to those in Figures 1,2,3 and 5.

General – additional details that would provide useful insight include how SO_2 and par-

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ticle sulfate were measured; the temperatures at which experiments were conducted; and whether any oxidant source was added (and how much) to initiate the oxidation of the hydrocarbons.

Technical corrections: The manuscript is largely free of typographical and grammatical errors.

L90 – an extra space in “by anthropogenic”

L109 – “of” should be “in”

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 29429, 2014.

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