Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2022-651

Anonymous Referee #2

Referee comment on "Yields and molecular composition of gas-phase and secondary organic aerosol from the photooxidation of the volatile consumer product benzyl alcohol: formation of highly oxygenated and hydroxy nitro-aromatic compounds" by Mohammed Jaoui et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-651-RC2, 2022

General Comments

This manuscript describes an experimental study of the reaction of benzyl alcohol with OH radicals in the presence and absence of NOx. Experiments were conducted in an environmental chamber under steady-state conditions, and gas and particle products were collected and analyzed using gas and liquid chromatography with mass spectrometry, without and with derivatization. Secondary organic aerosol yields were also measured. The measurements identified, and in some cases quantified, a large number of reaction products, and reaction mechanisms were proposed to explain their formation.

Overall, this is an impressive study and involved an enormous amount of work and careful chemical analysis. The results provide much more useful information on reaction products, including highly oxidized compounds and newly identified products, than can be obtained with more widely used online chemical ionization mass spectrometry methods. The detailed interpretation of the mass spectra that is presented is a bit tedious, but is important for structure assignments. It may be of interest to experts in such analyses or to others who would like to employ these methods. Considering the growing importance of volatile chemical products, such as benzyl alcohol, to organic emissions and atmospheric chemistry, and the high technical quality of the manuscript, I recommend it be published in ACP after the following comments are addressed.

Specific Comments

- Line 100: Stating that you used the highest purity compound available is not useful for assessing possible contaminants. Please state the purity.

- Lines 123, 181, 196: “Equilibrium” should be replaced by “steady state”. They are not the same.
- Line 135: How were these samples collected?
- Line 142: How did you correct the formaldehyde values for interference from the NO2-DNPH product?
- Lines 192–199: Please discuss the potential effects of gas-wall partitioning of benzyl alcohol and reaction products on your results in light of the modeling study of Krechmer et al. ES&T, 54, 12890, 2020.
- Line 220: What do you mean by “minimized”? Please provide a more quantitative description of the relative contributions of RO2 + NO and RO2 + RO2 reactions.
- Line 235: Does this wall loss rate account for differences in size distributions in different experiments?
- Line 248: What about possible reactions of benzyl alcohol with other species after partitioning to the walls?
- Line 285: What are typical derivatization efficiencies?
- Line 285: What happens to oligomers when they are exposed to derivatizing agents?
- Line 510: What are measured or estimated O3 and NO3 concentrations and how do you know they do not impact product composition?
- Since nitroaromatics are an important aspect of this study, I suggest reporting NO2 concentrations and discussing how they compare to the atmosphere. Formation of nitroaromatics involves competition between NO2 and O2, so if the NO2 concentrations in these experiments are unrealistically high, then the nitroaromatic products detected here are much less likely to be formed in the atmosphere.

Technical Comments

None.