Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2022-651-RC1, 2022

Comment on acp-2022-651

Anonymous Referee #1

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-RC1, 2022

This study focuses on the investigation of the benzyl alcohol photo-oxidation performed in a chamber. Species measured in the gas-phase included NOx, benzyl alcohol and low molecular weight carbonyls and dicarbonyls (by derivatization). Organic carbon in the aerosol together with aerosol volume, size distribution, and total number density were also measured. Finally, filter samples were collected for a non-targeted chemical analysis of species with hydroxy and carboxylic groups.

This study aimed to provide values for the SOA yield from the OH oxidation of benzyl alcohol as well as which oxygenated species are to be expected. In addition, a mechanism for the formation the observed oxygenated species is proposed.

The paper is well written and easy to read. It is reasonably organized and most of the section are clear.

The experimental part with the collection of the filters and the identification of the species in both the gas and the particle phase, although it is out of my area of expertise, seems thoughtfully done and described.

What is not convincing me is the proposed mechanism for the formation of the various species observed/identified. Following the recommendation of the authors I checked the study by Wang (2015) and I think more explanations are needed, in particular concerning the conditions of the experiments, to justify the suggested mechanism.

I would recommend publication after the following points are addressed:

- The study by Wang (2015) is applicable for atmospheric like conditions of reagents. This is not the case for the conditions in the smog chamber of this study where hundreds of ppbv of reagents are used. To justify the mechanism shown in Scheme 1 it is necessary to have a better understanding on the concentration of NO and NO_2 during the different experiments. NO can be sort of extrapolated from table 2 though it is less clear what the concentration of NO_2 The table lists NOy values but is that really NOy or is it NOx? I think the value of NO_2 is important as in the study by Wang (2015) it is stated that for high NO_2 (100 ppbv) the reaction of R1 (from Scheme 1) with NO_2 can compete with the reaction with O_2. If this is true, then the mechanisms proposed would only be part of the chemistry and the pathways following the reaction with NO_2 should be included.
- What is the rate of decomposition of R1-2OO and R2-1OO (from Scheme 1)? Wang (2015) calculate rates for the ring closure larger then $8x10^3$ s^{-1} for both isomers. The decomposition would have to be very fast to compete. In their study, (Wang, 2015) suggest that a possible path of formation for phenol and catechol could be the decomposition of R1, not R1-2OO. Although, even for R1 they seem to claim that their theory would mainly predict reaction with O_2 for R1.
- Which data/SARs are used for the mechanisms proposed for the reactions of R1-26OO and R2-1300? I understand it is derived based on similarities with other species but it would be good to give a little bit more details about how it is derive and if this is one possible mechanisms and other paths could also contribute. Also, I assume NO_2 in scheme 3 should be NO?

I think overall trying and suggest mechanisms for the formation of the different species is valuable and of interest but it should be done carefully and considering the conditions of the experiments and what from the literature can be applied.

Minor/technical comments:

Section 2.5: I think a little bit more details on how experiments are performed would be beneficial. For example, what is the purity of the synthetic air used in the chamber? When are the reagents injected and how long is the waiting before the background is measured?

Page 9, line 220: since the NO is high so that RO_2+RO_2 reactions are minimized, why is in scheme 3 indicated that RO_2 could be a reaction partner?

Page 10, line 224: how is BnOH going to react with NOx?

Page 10, lines 225-226: is there a way to separate the yield of SOA from the introduce concentration of SOA? As the yield should be used in models and it would need to be independent on the concentration of SOA, I assume?

Page 10, line 260: for consistency, it would be good to use the same expression for the yields, either as a fraction or as a percentage.

Page 14, line 373-373: catechol on one line is mentioned to be observed for both conditions of NOx while in the following line it is mentioned only for experiments without NOx?

Wang, L.: The Atmospheric Oxidation Mechanism of Benzyl Alcohol Initiated by OH Radicals: The Addition Channels, Chemphyschem, 16, 1542-1550, doi:https://doi.org/10.1002/cphc.201500012, 2015.