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Discussions

Interactive comment on "Secondary Organic Aerosol Yields from the Oxidation of Benzyl Alcohol" *by* Sophia M. Charan et al.

Anonymous Referee #2

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Review of "Secondary Organic Aerosol Yields from the Oxidation of Benzyl Alcohol" by Charan et al.

Synopsis.

The researchers embark on an investigation of volatile consumer products (VCPs) and for the initial compound they consider the photooxidation of benzyl alcohol (BnOH). The experiments are run with NOx present in the system and at levels there are using virtually all the peroxy radicals formed react with NO to form alkoxy radicals. While the experiments are suitable for examining ozone formation, the authors have decided to focus on SOA formation. A chemical ionization mass spectrometer (CIMS) is adopted for measuring gas-phase oxidation products. For particle measurements, particularly for determining aerosol yields (Y), a scanning mobility particle analyzer (SMPS) has

been used to measure particle volumes which can then be converted to particle mass using a density (1.4). The results indicated extremely high yields for BnOH ranging from 0.35 – 1.0. The authors then examine values for the yield for as a function of several parameters important in atmospheric scenarios, such as NOx levels, temperature, amount of BnOH reacted, and seed surface area.

An extensive discussion is given regarding the effect of walls on the deposition of condensable organic compounds to particles lost to the chamber walls to provide a corrected yield, ω (gk: omega). This turns out to be a negligible correction compared to the uncertainty of the SOA yield determination. Following this additional wall corrections are enumerated and (presumably) justified. The most important is the actual particle loss to the chamber. This second correction is very important to the interpretation of the work because it leads to the authors selection of the ammonium sulfate (AS) aerosol seed surface area (and by extension mass) that the authors select for their experiments. They also consider gas-phase product loss to the walls but ultimately decide that it is unimportant. When all is said and done the extent of the corrections to particle loss is 10 – 20%. Ultimately, the authors conclude that an aerosol yield as a function of time converges on a single value for the parameterization considered and becomes independent on the amount of BnOH reacted.

The paper ends up by considering gas-phase mechanism relevant to the degradation of BnOH and possibly to aid in interpreting these very high yields, but sadly as the authors note (line 391), the considerations in Section 6 do not affect the SOA yields. However, the section does give some clue as to the plausibility of the reported results.

General comments.

This paper caught my eye from the SOA yields approaching unity under some conditions. The results certainly merit publication and the authors have generated a fairly comprehensive dataset for yields with NOx present under a reasonably wide set of conditions. However, I do believe that the paper needs considerable work to entice physical scientists to read it and appreciate the significance of the results. My main comments will address organization, emphasis, assumptions, and consistency, in no particular order.

(1) I believe that much of the message and findings of the paper are lost in the inordinate focus on corrections to the calculated yield in Section 3. For example, we have a reasonably detailed discussion of the factor ω (loss of condensable organic products to particles on the chamber walls) only to find out on line 200 that this factor is basically irrelevant to the yield determination. For me, this comment suggests that this section is essentially appendix material. All of Section 3 really needs to be reduced to one or two pages. The only section that should be discussed in any detail is Section 3.2.1. Otherwise, just give the major findings from the section.

(2) The justification for use AS seed aerosol with very high surface areas is to compete for condensable organics with losses to the walls. This leads to a seed aerosol concentrations having masses probably 10 – 100 times that found in the atmosphere. These conditions limit the relevance of these experiments to atmospheric conditions. However, I am more worried about the mechanism for SOA formation at high surface areas. In the atmosphere, adsorption of organics while present cannot compete with absorption of condensable organics into the organic mass already present. I wonder if this is the case in the present experiments. At these high surface areas, can the major process for SOA condensation be adsorption and not absorption. I think this is a subject that should be discussed in the paper or at least explicitly discounted by performing the necessary calculations.

(3) Are these results consistent with the partitioning approach developed at Caltech in the mid-1990's. Can these results be expressed in a two-product model described by Odum et al. (1996, 1997) with appropriate updates from Ng (2007) and possibly others?

(4) The error analysis needs to be addressed in more detail. Starting with the first figure, the most striking thing in the figure is the magnitude of uncertainty associated with the yield for this experiment. If this is representative, and presumably it is, it is likely due to random errors rather than systematic errors, since they are already discussed extensively in Section 3. Thus, it appears to me that the random error completely swamps out the systematic error. I am not sure how the authors expect to convince a modeler of the accuracy with this level of uncertainty. Is it possible that these considerable random errors are due to a relatively small SOA mass condensing onto seed aerosol of considerably higher mass leading to errors associated with the subtraction of two large numbers? The issue of random errors needs to be better addressed in the text.

(5) Section 4 seems to be an appendage to the paper. It adds little to the interpretations in the paper, is not mentioned in the Abstract or Conclusions, and for me distracts from the main message of the paper. Unless these results can be better incorporated into the yield consideration or perhaps in the mechanism discussion of Section 6, I would remove it from this paper, and perhaps base a separate paper on this data. As an alternative, can the data in Section 4 be used in conjunction with the mechanistic discussion of Section 6, in which case I would place it immediately before Section 6.

(6) I find much of Section 6 to be of little value the way it is currently presented. As noted earlier, the authors state that the actual composition of products is decoupled from the yield measurement. Thus, this section is more of academic interest than anything else. The photooxidation of BnOH in the presence of NOx simply follows analogous with mechanisms for photooxidation of toluene in terms of abstraction from the substituent group and addition to the aromatic ring.

(7) A mass balance estimation of measured and likely products from the NOx photooxidation of BnOH make it implausible that yields approaching unity are realistic. The mechanism of BnOH oxidation with NOx is reported to give benzaldehyde as a major product with a yield of 0.25 (Harrison and Wells, 2009; Bernard et al., 2013; see author refs). And yet the authors states on line 463 that benzaldehyde does not form condensable products. Benzaldehyde together with small ring-fragmentation products

also unlikely to give condensable products probably make up at least 50% of the initial reacted BnOH mass. With half of the mass unavailable for SOA formation, it is hard for me to justify SOA yields of 1 and greater. Moreover, Figure 14 suggests that an extrapolation to atmospheric BnOH levels would make the effective yield substantially greater than 1. Where is all the SOA mass coming from? It seems to me that this is a serious issue that the authors need to address.

(8) Two important parameters not tested are wet AS (metastable AS along the deliquescence curve; important for summertime SOA formation) and SOA yields in the absence of NOx. In addition, limitations for modeling the reported yields might be mentioned in the discussion or conclusions.

Some detailed comments by line number or other identifier.

Line 43 – Please comment on this sentence in the conclusions. Are the authors using the word “result” to mean BnOH SOA yield?

Line 65 – Since H2O2 absorbs to a negligible degree at 350 nm, it would be useful to know the value for the radiation output at FWHM of the blacklight source. It seems to me that the photolysis rate for H2O2 is of as much, if not more, value than that of NO2 given the initial conditions.

Line 96 – How about a consideration of systematic errors for the BnOH measurements? Also, if I understand this sentence correctly, Table 1 gives the variance of the reacted BnOH together with the initial BnOH. Why not simply have an additional column with the value for the reacted BnOH together with its variance, or is the claim that the variance in the reacted BnOH associated solely with its initial concentration?

Line 120 – This sentence comes out-of-the-blue? Can a reference be added?

Table 1 – A column for the initial NO2 concentration is desperately needed. Delete the final column if room is needed. (See below) The double-dagger appears to apply to all data in that column; is that correct? For column 7, what is the origin of the value for

[OH]?

Lines 176-198 – Most of this material should be relegated to an appendix which is already being used in this paper or a supplementary information section. The correction is of little use as noted.

Figure 1. Is the uncertainty shown in the grey for Panel (a) representative of all experiments? If so, a more critical discussion of this is needed. What experiment in Table 1 is represented in this figure?

Line 242 – Why is there a need to make an assumption? Is not the aerosol volume being measured during the background measurements?

Section 3.2.2 – This looks like another section for an appendix or SI, since this correction is not used in any fashion as noted in lines 273-275.

Table 2. Are the uncertainties given consistent with the random error shown in Figure 1a?

Section 4. I would move this section to that after Section 5 and try to tie this data to the discussion of the chemical mechanism.

Line 289 – Given that mass-transfer-limited is mentioned several times in the text, it would be valuable for the authors to give their explanation of the term. Is this term equivalent to saying that SOA formation is kinetically controlled?

Line 294 – What sort of particle-phase reactions do the authors have in mind? Oligomerization? Figure 3b. Why is the noise in this panel so much greater than in the other two? Figures 3 and 4 add little to the discussion of the reported yields and might be considered for elimination.

Figure 6. This figure is meant to be associated with Figure 5 but does a poor job doing so. I would simply give the [BnOH] at 200 minutes. And at what point does the system run out of NO? This may be the reason that more condensable products are

not produced after 100-200 minutes.

Figure 7. Could this figure be interpreted as showing that partitioning is occurring. Perhaps a figure of Y vs. M0 would be informative.

Figure 8. I see no evidence in the experimental section as to how the temperature of the chamber is controlled to allow this data to be obtained. Moreover, how is the temperature in the chamber held constant as the irradiation proceeds when radiative heating from the lights is continuously occurring? As I read the figure, a 20-degree increase in temperature reduces the yield from 1.0 to 0.4. Seems like a substantial effect.

Line 383; 393 – I would not call a description of the photooxidation of BnOH a theory. The “theoretical value” for benzaldehyde formation (29.6%) from Wang (2015) is based on assuming the branching ratio from the abstraction channel is 25% (Bernard et al., 2013) and then adding 4% from the OH-addition to the substituted position of the aromatic ring (the subject of the paper) determined by quantum chemistry calculations – hardly a theoretical value.

Figure 10. For the scheme presented here, I would explore the possibility of NO2 adding to the initial cyclohexadienyl radical to compete with O2 addition given in the third channel (0.41). I only mention this because nitro hydroxyaromatics could easily partition into the particle phase and could be amenable for detection by AMS.

Section 6.2. This model is largely an exercise in data fitting. A discussion of the important adjustable parameters and any physical significance would be appropriate. I’m not sure this section adds very much to the paper.

Line 423. Delete the word “precisely”. I am not sure what the difference is between ‘constrained’ and ‘precisely constrained’. In my view, the model is better characterized as unconstrained. My opinion of Section 6.2 is that it detracts from the main subject of the paper.

Figures 11 & 12 and Table 4. I would consider these as appendix-type materials even if Section 6.2 is to remain in the paper.

Line 463. Given the unconstrained nature of the aerosol model for the chamber, it does not surprise me that an effect from possible SOA products from benzaldehyde cannot be detected. This question (or assumption) regarding condensable products from benzaldehyde photooxidation is probably best addressed experimentally. Why not just do a photooxidation experiments using benzaldehyde as the reactant rather than BnOH? Note: I am not asking for additional experiment(s).

Figure 14. If the yield from this figure is extrapolated to ambient BnOH concentrations, a value of 2 or more would need to be used. Hardly seems plausible, especially since 25-50% of the BnOH products are non-condensable and given the yield McDonald uses of 0.09. Thus, these experiments would suggest that the yield should be increased by a factor of 20.

Line 503. Some text should be added to the appendix at least referring to Figures A1 and Table A1.

Line 546. Some indication of the availability of this report should be provided, if possible.

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