

Interactive comment on “High formation of secondary organic aerosol from the photo-oxidation of toluene” by L. Hildebrandt et al.

L. Hildebrandt et al.

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AUTHOR COMMENTS

The authors would like to thank the two anonymous reviewers and Quentin Malloy for their helpful comments and suggestions. All comments are addressed below. Comments are also included below.

Response to Referee # 1

Specific Comments

Comment 1

Page 696: A very recent study by Cao and Jang (2008) provides some new data on the effects of acidity on the yield of SOA from the photooxidation of toluene. It would

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be appropriate to incorporate these results into the introduction.

Response 1

While Cao and Jang observed an effect of acidity on organic aerosol yields, the acidities used in their experiments were very high. Therefore, we believe that the statement that "The organic aerosol yields do not seem to be affected by acidities typically found in the atmosphere." is still accurate. Unfortunately, the Cao and Jang (2008) study was not selected for publication in ACP. Therefore, we decided not to include a detailed discussion of their findings in this manuscript.

Comment 2

Pages 697-698: There are a number of important details missing from the experimental section. Was hydrogen peroxide used in all experiments, including those with high NO_x levels? How much hydrogen peroxide was added to the chamber? What was the mass concentration of seed aerosol in the experiments? If some of these parameters varied from experiment to experiment, then it may be more appropriate to include them in Table 1.

Response 2

Yes, hydrogen peroxide was used in all experiments; we have made this more explicit in the text. Hydrogen peroxide is used in great excess, which is necessary because the emission spectrum of the lights and the absorptions spectrum of hydrogen peroxide only overlap partially. Due to this excess of hydrogen peroxide present, we do not expect the initial hydrogen peroxide concentrations to have an effect on the aerosol yield.

Nevertheless, we have added the H₂O₂ concentrations used in Table 1. An additional advantage of the high H₂O₂ concentrations, is to 'condition' the HO_x-RO_x chemistry toward HO₂, more consistent with atmospheric HO_x-RO_x partitioning (Kroll et al., 2008). We have also included the initial seed concentration in Table 1, which also varied be-

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tween experiments. The purpose of the seed aerosol is to provide surface area onto which the organic vapors can condense.

Comment 3

Page 701, line 16: It is assumed that the wall deposition constant of the organic material is the same as that of the inorganic material. Could an experiment be performed to confirm this? For example, the deposition of SOA produced via nucleation in the absence of seed aerosol could be compared against the deposition rate of the pure seed.

Response 3

We agree that the assumption that the wall deposition constant of the organic material is the same as that of the inorganic material introduces a small error in our calculations. As discussed in the paragraph on pages 708/709 of the ACPD manuscript, the presence of an offset in the size distribution of the organic material and the inorganic material suggests that organic material is probably lost at a slightly higher rate than inorganic material. We estimate that the error introduced by the assumption of a common wall deposition constant is only a few percent. This error is expected to result in a negative bias of the reported organic aerosol mass yields.

Nucleation experiments often produce aerosol with quite different size distributions than "seeded" experiments, mostly because nucleation results in more and smaller particles than condensation onto seed particles. These small particles can be lost very efficiently to the chamber walls; hence, the comparison between nucleation and seeded experiments will not be a very useful test.

Comment 4

Page 711, lines 18-28: The authors compare experiments 1 and 2 to show that a higher SOA yield was obtained with higher UV intensity. This effect has also recently been reported for the photooxidation of m-xylene, and has been attributed to higher

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OH levels which cause a faster decay of the parent hydrocarbon and more rapid SOA formation (Warren et al., 2008). It is therefore somewhat surprising that the authors observed no significant difference in the decay rate of toluene between experiments 1 and 2. However, closer inspection of the data reported in Table 1 shows that the initial conditions are in fact quite different and one may expect that the OH levels and thus the toluene photooxidation rate may be quite different anyway. Thus it is possible that any difference in the toluene decay rate attributed to the change in UV light intensity may be offset by the change in decay rate due to different levels of toluene and NO_x. In my opinion, it is not entirely appropriate that these two experiments be compared directly compared in this manner. Regardless, it is important that the authors address and clarify this matter in the revised manuscript.

Response 4

There seems to be a misunderstanding. We are comparing experiments 1 and 3 (not experiment 2) to show that a higher SOA yield was obtained with higher UV intensity. Experiments 1 and 3 have very similar initial toluene concentrations (940 ppb and 950 ppb, respectively). We acknowledge that the level of NO_x in these experiments is different: the initial VOC/NO_x ratio in experiment 1 was 5.1 (ppbC/ppb), and 12 in experiment 3. We consider the conditions in both experiments to be "high NO_x" and therefore would not have expected such a significant difference in aerosol yields.

We also find it interesting that OH concentrations did not increase significantly with increased UV. However, this observation is consistent with a number of earlier experiments that we conducted under the lower UV conditions (not reported in this study) in which we did not observe lower OH concentrations than in the later experiments conducted under higher UV conditions.

We cannot measure OH levels directly but rather estimate it by the first-order decay of toluene in the PTR-MS. We have added this estimate of the average OH concentration in the experiments presented here in Table 1.

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Comment 5

Page 712, lines 13-22: As reported in other studies, higher SOA yields are obtained under low NO_x conditions. However, the recent work of Cao and Jang (2008) showed that, under high NO_x conditions, the relative starting concentrations of NO and NO₂ have a profound effect on yield, with significantly higher yields obtained when the initial concentration of NO₂ was higher than NO. It would therefore be instructive to report initial NO and NO₂ concentrations in Table 1 for comparative purposes.

Response 5

We added no NO₂ to the chamber and started the experiment with NO only. We have made this more explicit in the revised manuscript. All NO was quickly converted to NO₂ (see comment 6).

Comment 6

Page 715, lines 9-13: It is reported that most of the NO is quickly converted to NO₂ within a few minutes of turning the lights on. This is somewhat unusual in high NO_x experiments, where the decay of NO generally takes the order of tens of minutes. What is the reason for the very rapid conversion? Is hydrogen peroxide also present in the high NO_x system? This produces lots of HO₂ which may accelerate the conversion of NO to NO₂.

Response 6

Yes, we added hydrogen peroxide in all experiments (see response to comment 2), and we believe that this is the reason for the rapid conversion of NO to NO₂.

Minor Comments

1. Page 696, lines 1-7: Song et al., (2007) report that, contrary to expectation, propene does not enhance OH levels in chamber studies - it reduces them. This part of the text should be changed accordingly.

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Response: We modified the text in the revised manuscript.

In addition, "Takekawa" is spelt incorrectly in line 5.

Response: Fixed.

2. Page 697, line 11: End sentence after "oxidation".

Response: Fixed.

3. Page 699, line 19: The company name is "Vaisala".

Response: Fixed.

4. Page 711, line 7: Remove second "not".

Response: Fixed.

5. Page 717, line 32: The correct representation for ammonium sulfate should be $(\text{NH}_4)_2\text{SO}_4$.

Response: Fixed.

6. Page 718, line 4: First author is "de Gouw".

Response: Fixed.

7. Page 718, line 17: Change "nox" to "NOx"

Response: Fixed.

8. Page 719, line 13: Remove capital letters in the title of this paper.

Response: Fixed.

9. Page 727, figure 4: Change "communication" to "interaction" in the figure caption.

Response: Changed.

10. Page 729, figure 6: Change "communication" to "interaction" in the figure caption.

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Response: Changed.

Response to Referee # 2

Comment 1

p. 695, l. 20 ff. and also in the discussion of your experiments: It is not the absolute NO_x level but the ratio of RO₂/NO that determines the branching ratio in the gas phase. Could you report this ratio - or in a first approximation the ratio of toluene/NO - that has been used in previous studies and in comparison to your experimental conditions?

Response 1

We have added some discussion of the initial toluene/NO and toluene/NO_x ratios to the experimental section. This additional information emphasizes the wide range in experimental conditions that have been employed in these experiments.

Comment 2

p. 696, l. 26/27: This sentence does not seem correct as it is since recent work has shown that organic aerosol mass does increase with increasing relative humidity and/or liquid water content (e.g., Volkamer et al., ACPD, 2007; Hennigan et al., GRL, 2007). To be more correct you should rephrase saying "Aerosol formation by semivolatile compounds seem to be dependent".

Response 2

To avoid misunderstandings this part of the text has been changed to: "The amount of liquid water in the aerosol seed also appears to affect the aerosol mass yield, but the magnitude of this effect remains uncertain (Edney et al, 2000; Hennigan et al., 2008; Volkamer et al., 2009)."

Comment 3

p. 698, l. 23: What structure can you ascribe to m/z = 39?

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Response 3

With the Q-AMS, which only provides unit mass resolution data, we cannot ascribe a structure to $m/z = 39$, nor a molecular formula. We have since conducted a toluene photo-oxidation experiment measuring with a HR-Tof-AMS, with which we can ascribe a molecular formula. The mass we observe at $m/z = 39$ is due to C_3H_3 . We presume that this is a radical or cyclical fragment resulting from electron ionization in the AMS, which is a rather hard ionization method.

Comment 4

Experimental section: Have all experiments been carried out at dry conditions? If not, at what RH?

Response 4

We started all experiments by filling the chamber with dry air. Since the H_2O_2 was in solution with water, introducing H_2O_2 into the chamber also introduced water vapor. Thus, the RH of the experiments presented here ranged from 5 to 21%. We have added this information to Table 1.

Comment 5

p. 707, l. 15: Is the time scale of ageing the same under atmospheric conditions or is it slowed down due to smaller oxidant concentrations? How important is the "several generation" ageing under atmospheric conditions?

Response 5

Even though we do not measure OH directly in these experiments, the inferred oxidant concentration (from observing the toluene decay rate) is similar to atmospheric conditions (see Table 1). Therefore, the time scale of ageing in these experiments is similar to atmospheric conditions. The multiple generation ageing may be even more important under atmospheric conditions since total VOC concentrations are lower than

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in these experiments and, therefore, competition for OH is smaller.

Comment 6

p. 708, l. 15; l. 21: The term "internally mixed particle" seems misleading since it might imply that organics and sulfate are homogeneously mixed whereas a coating suggests rather a heterogeneously mixed particle. Clarify the use of "internal mixing" here.

Response 6

We have clarified this in the revised manuscript. We have deleted the use of "internally mixed" in l.15. Instead, we have modified the first sentence of this paragraph to read: "The suspended particles form a partial internal mixture: all particles consist of ammonium sulfate cores coated with toluene-derived SOA, but the organic to sulfate ratio is a function of the particle size."

Comment 7

p. 711, l. 25: (i) What are the OH levels in the chambers? Are they comparable to atmospheric levels?

Response 7 (i)

Yes, they are. We have included an estimate of the OH levels in Table 1.

Comment

(ii) In the atmosphere there are many more sinks for OH than just toluene. Thus, does the photolysis rate of 0.18 min^{-1} result in the same OH levels as in the atmosphere?

Response 7 (ii)

It is true that there are many more sinks for OH than just toluene in the atmosphere. However, it is the total first-order loss rate of OH, and also the net sources and sinks of HO_x, that controls OH levels. The atmosphere has a rich array of HO_x sinks whereas our system is dominated by toluene and its oxidation products. In the end, OH levels in

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the chamber are similar to OH levels typical of urban environments ($1\text{--}3 \times 10^6 \text{ cm}^{-3}$). Secondly, we want to clarify that the 0.18 min^{-1} is the photolysis rate of NO_2 (to NO). Thus, it is not a direct measure of OH formation but is rather a measure of the light intensity in the chamber.

Comment 8

p. 712, l. 27 and Fig. 7: It looks like a very steep increase of the %44 signal in the first few minutes. (The first point seems to be lower than the following ones). If this is real, could you comment on it and quantify the time scale of that step increase?

Response 8

The rather steep increase of the %44 signal in the first few minutes is only partially due to changes in the organic aerosol from toluene. The introduced inorganic seeds include a very small amount of organic contamination. The magnitude of the organic seed contamination scales with the initial seed mass and while small during the first few minutes of the experiment, it dominates the organic aerosol composition. This is why the total organic aerosol composition changes, but why that change is not reflective of changes in the organic aerosol from toluene. We have adjusted the organic aerosol yields for this small organic contamination, but we have not attempted to adjust the relative organic spectrum.

Comment 9

p. 713, l. 27: How do your measured %44 percentages compare to ambient aerosol samples?

Response 9

Ambient aerosol samples exhibit a wide range of %44 values - from less than 5% to ~25% (Aiken, 2008). We have added this information to the revised manuscript. Only very aged aerosol can have %44 values up to 25% - the fresher SOA usually has %44 values below 15%. Thus, the %44 values observed in our experiments compare well

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with %44 values observed in fresher ambient aerosol samples.

Comment 10

p. 714, l. 12: What are the reasons for the changing product distribution? Is it because reaction rates are enhanced at higher temperatures that convert species into products with different %44 content or is it rather evaporation of "high %44" species and leaving behind "low %44" species?

Response 10

Unfortunately, the gas-phase reactions leading to SOA from toluene are poorly understood, and our limited gas-phase measurements are insufficient to answer this question conclusively. We presume that the primary reason for the different product distribution is not the gas-phase chemistry, since reaction rates with OH are only modestly dependent on temperature. The particle-phase explanation is very reasonable: we expect net condensation (condensation - evaporation) of "low %44" species to be lower than that of "high %44" species. This is because "low %44" species are less oxidized and therefore often have a higher vapor pressure, making them less likely to condense to the particle phase and more likely to evaporate than the "high %44" species.

Comment 11

p. 715, l. 10: The fact that in your system all NO is quickly converted into NO₂ does not resemble atmospheric conditions where NO can be a significant fraction of NO_x. Thus, it seems to me that under those conditions the yields reported by Ng et al. are more appropriate.

Response 11

We agree that a mixture of NO and NO₂ more closely resembles typical atmospheric conditions, and that the experiments by Ng et al. capture better this aspect of the system. We have added this to the text of the revised manuscript.

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Comment 12

Conclusions: It would be very useful if you could add in the conclusions some quantification on how much each of the three factors (UV light conditions, AMS vs. SMPS, and wall losses) has changed the yield as compared to previous results. In addition, some error estimate would be useful as well.

Response 12

We do not yet have an accurate chemical mechanism including multiple generations of toluene oxidation in both the gas and condensed phases. Consequently, it is difficult to establish which of the various factors (UV, OH levels, T, etc) are responsible for differences between our results and others in the literature. It would be possible to construct many different potential scenarios by taking the dependencies we determine empirically with respect to these various variables, but it is not at all clear that this would advance our understanding. Clearly, we would like to develop at least an empirical mechanism to describe the dependence and evolution of SOA on atmospherically relevant variables, but we see the role of this paper being simply to establish that the dependencies are present.

The average experimental error could be estimated by comparing the results of experiments conducted under similar experimental conditions. Using this method Pathak et al. (2007) estimated an experimental error of +/- 10% for SOA yields in the CMU smog chamber. Comparing our measured yields for experiments 11 and 12, which were performed under very similar experimental conditions, the discrepancy in the experiments presented here also appears to be within 10%. We hence estimate an experimental error of +/- 10%, and we have included this information in the revised manuscript (Section 3.1).

Technical comments

I. 717, I. 9: "Worsnop" misspelled.

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Response: Fixed

I. 717, l. 12 : "measurement" misspelled.

Response: Fixed

I. 718, l. 10: "secondary" misspelled.

Response: Fixed

Response to Quentin Malloy

Comment:

On page 711 the author states the toluene decay rate was unchanged for the two different light intensities examined. However, a recent paper by Warren et al. has shown that light intensity affects the rate of decay for the m-xylene/NO_x photo-oxidation system, which one would assume would be similar to the toluene system studied here. It would be interesting for the author to expand on their analysis of their findings given this discrepancy.

Response

We did not measure OH concentrations directly. Instead, we estimated [OH] levels from the first-order decay of toluene observed in the PTR-MS. We have added this estimate of the average OH concentration in the experiments presented here in Table 1. We also find it interesting that OH concentrations did not increase significantly with increased UV. However, this observation is consistent with a number of earlier experiments that we conducted under the lower UV conditions (not reported in this study) in which we did not observe lower OH concentrations. A possible reason is accelerated reactions of OH with the products of the toluene photooxidation.

References:

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