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Atmospheric
Chemistry
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Discussions

Interactive comment on "Secondary organic aerosol formation from toluene photooxidation under various NO_x conditions and particle acidity" *by* G. Cao and M. Jang

Anonymous Referee #1

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This study investigated the effect of NOx, humidity, and seed acidity on SOA formation from the photooxidation of toluene. Experiments were conducted at three different NOx levels (low, intermediate, and high NOx conditions); at each NOx level high/low RH and acid/neutral seed experiments were performed. It is found that both acid effect and humidity effect depend on the NOx level in the experiments. Under high NOx conditions, no significant acid effect and humidity effect are observed.

Recent studies have shown that SOA formation from aromatic hydrocarbons is highly dependent on the NOx levels; this work investigated two other important parameters (RH and acidity) which are essential to help us further understand the aerosol formation from aromatic hydrocarbons. However, there are a number of issues that need to be addressed before the paper can be published.

One issue involves the relevance of these experiments to the atmosphere. The majority of the experiments were conducted under high initial seed concentrations and possible high toluene concentrations. The results from the two experiments with more realistic concentrations, however, showed a much smaller difference in yield between acid and neutral seeds. This raises the concern of whether one can apply the results from this study to atmospheric conditions. The authors would probably have to re-run some experiments under more atmospherically realistic conditions to make this study more convincing.

Another issue lies in the interpretation of the results. To unravel the complicated effect of NOx, acidity, and humidity on SOA formation is certainly not easy; and in many cases the authors' interpretations of the experimental results seem confusing and inadequate. Many of the explanations remain qualitative. For instance, the authors should make an effort to estimate the relative importance of the various reaction pathways of RO2 radicals under different experimental conditions. Also, it appears that the water content of the particle plays an important role in aerosol formation. One should be able to estimate the water content in the aerosols with ISORROPIA and such information should be included in the manuscript.

Finally, I do not think that the results from the high NOx experiments are correctly interpreted. The authors divided each high NOx experiment into a "high NO fraction" and a "low NO fraction", they then calculated the "yield" separately and compared them to other experiments. In these high NOx experiments, there is a switch of NOx conditions over the course of the experiment, the products formed are essentially a mixture of the products under different NOx conditions and I do no think that the authors can simply divide up the experiments into two different periods. For details please refer to the specific comments below.

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Overall, this work should be published eventually, but only after all the issues have been carefully addressed.

Specific comments:

1. Page 14471, line 12. The volume of the chamber is 2 m3. In such a small chamber the loss of particles to the chamber wall is significant. How is wall loss corrected for and how much aerosol growth is "added back"(compare to the amount of aerosol growth reported)?

2. Page 14471, line 27. The authors should specify the concentrations of the solutions used.

3. Page 14472, line 24. As the authors pointed out in Page 14477, in the low RH experiments the neutral seed is solid (since the RH used is lower than the efflorescence RH of ammonium sulfate). How does one define "proton concentration" in a solid seed?

4. Page 14473, section 3.1.1. The authors described the various channels for RO2 reactions under different NOx conditions. However, they need to be more quantitative here. The authors wrote "Channels A and B are the dominant pathways under low NOx conditions, while channels C and D are significant under the intermediate and high NOx conditions....for the intermediate NOx conditions, channel C is likely the dominant pathway to convert NO to NO2 and generate carbonyls". Under low NOx condition, I would think only RO2+HO2 is significant given the high concentration of H2O2 used. Under the intermediate NOx conditions, are the authors sure that RO2+NO-> RO+NO2 dominates over RO2+NO->RONO2? The authors should at least make a quick estimate on the relative importance of different channels based on the reactive rate constants of RO2 with RO2/HO2/NO.

5. Page 14476, low NOx conditions. This section is quite confusing.

a. The authors reported an enhance SOA formation with acidic seeds under both high and low RH experiments. It is suggested that the additional SOA formation is a result of heterogeneous acid-catalyzed reactions or organics sulfate formation. Under low NOx conditions, the RO2+HO2 reaction dominates and organic hydroperoxides should be the major products. The authors later wrote "the formation of peroxyhemiacetals in the particle phase reactions between a hydroperoxide and an aldehyde may be relatively not sensitive to the particle acidity but to WV in the system" - If this is the case, do the authors have any suggestion on what type of heterogeneous reaction may be in play here and result in the enhanced yield?

b. Ng et. al. (2007) studied SOA formation from aromatic hydrocarbons but the authors did not observe any significant increase in SOA formation under both high and low NOx conditions (and RH$<$10%). The authors should comment on the difference.

c. Page 14477, line 1. The authors wrote "secondarily, heterogeneous reactions of carbonyls (e.g. heterogeneous acid-catalyzed reactions or organic sulfate formation) are responsible for the higher SOA yields in the presence of acidic sulfate seed aerosols compared to those in neutral seed aerosols" - I thought in this paragraph the authors were discussing the difference in yield between low and high RH experiments. However, this "second" reason seems to apply to the difference in yield between acid and nonacid experiments instead.

d. Page 14477, line 6. The authors wrote "Thirdly, the partitioning processes may be influenced by WP particularly for hydrophilic products". How would this explain the higher aerosol yield observed in low RH experiments? As the authors pointed out before (Page 14476, line 8): "More water content in the particle at high %RH can facilitate partitioning of hydrophilic products resulting in more SOA production" - if this is true, shouldn't we expect more SOA formation in the high RH experiments?

6. Page 14478, high NOx conditions. The authors divided each high NOx experiment into "high NO fraction" and "low NO fraction". When looking at Table 1, it is not clear that each pair of high NOx (high NO fraction and low NO fraction) experiments are actually one experiment. This is very confusing, as they look like different experiments with

different initial NO concentrations. I do not think that the authors can "break down" the experiments this way and report two different yields (high NO fraction and low NO fraction) for each experiment. In doing so, the yields reported for the high NOx (high NO fraction) are essentially "instantaneous yields" (as toluene is still reacting at that point) and cannot be compared with yields in other experiments. Furthermore, the "seeds" in the high NOx (low NO fraction) experiments already have organics - the presence of organics increases partitioning and increases aerosol yields; hence the yields obtained cannot be compared to other yields either. It is true that as the high NOx experiment progresses, the experimental condition changes from high NOx to intermediate NOx to low NOx; such a switch in NOx conditions makes it difficult to evaluate the effect of NOx on SOA formation as the fate of peroxy radicals is constantly changing. The products formed would a mixture of the products under different NOx conditions. Hence, the authors cannot simply break down the experiments into two parts and calculate the yield for each section. When combining the two sections together (high NO fraction and low NO fraction), the SOA yield is about 11-13% for the four high NOx experiments. Based on these results, I think at most the authors can conclude that there is no significant humidity effect and acid effect under high NOx conditions, and nothing more than that (I do no think that it is meaningful to compare the yields from the high NO fraction and low NO fraction to other experiments and interpret the differences).

7. Page 1440, line 25 onwards and Figure 5C. In Figure 5C, there is a change in the shape of growth curve, at approximately Del ROG = 600 ug/m3. The authors suggested that "this is likely because large amounts of nitro products existed in the system at high NO2 concentrations and the gas-particle partitioning of nitro products act as the dominant pathways for SOA formation". I suspect this is not the case. Several studies have shown that the reaction of the aromatic-OH adduct with NO2 is not significant even in the presence of many hundreds of ppb of NO2 (Volkamer et al., 2002; Koch et al., 2006). The authors did not show the time profiles for the NO and NO2 concentration (I suggest them to do so in the revised manuscript), however, I would guess the "kink" in the time-dependent growth curve is the time when [NO] approaches zero. At that

time, there is a change from high NOx to low NOx condition; hence the RO2 mainly reacts with HO2 to form more non-volatile products.

8. Page 14481, section 3.3. I have a few comments regarding this section.

a. How do the time-dependent growth curves for the two atmospherically relevant experiments look like? The difference in yield (12.5%) seems pretty small compared to the uncertainties in yield. The authors need to make sure that such a difference is observed throughout the experiment, but not due to scatter in certain data points. Also, as pointed out before, in small chambers where wall loss plays a significant role, the authors need to be careful in interpreting the experimental results, especially in situations like this where the difference in yield is small relative to the uncertainties.

b. It appears that the authors were aware of the fact that most of the experiments were conducted with concentrations (toluene concentrations, seed concentrations) that are too high to be atmospherically relevant. If they were able to conduct experiments under conditions more relevant to the atmosphere (Table 4), why are the majority of the experiments conducted with high initial seed volumes (and extremely acidic seed) and high toluene concentrations (Table 1)? In fact, what is the initial concentration of toluene in the chamber and how much is left at the end of the experiment?

c. This is related to the previous point. According to Ng et al. (2007), it appears that there are multiple oxidation steps in SOA formation from aromatic hydrocarbons; SOA formation from the condensation of first-generation products is not excluded, however, it does appear that higher generation products contribute significantly to aerosol growth. Given the relative slow reaction of toluene with OH, I would imagine the initial concentration of toluene in the chamber is pretty high. Under such conditions, the first-generation products may have a difficult time competing with toluene for the OH and further oxidations would be suppressed. How would this affect the SOA formation in these systems and the conclusions of the this study?

d. Under similar conditions (intermediate NOx, high RH), the difference in yield be-

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tween the acid and neutral seed in Table 3 is 44%, yet the difference is only 12.5% when more realistic concentrations are used. What does this imply about the other experiments that are conducted at high toluene and seed concentrations (and seed acidity)? I am not sure if one can assume the results in Table 3 can be extended to atmospherically realistic conditions.

9. Table 1. The author should not divide the high NOx experiments into "high NO fraction" and "low NO fraction".

10. Table 2. When calculating the percentage difference, it is better if the authors use the SOA yield at low NOx as the denumerator in all cases.

11. Table 3. How did the authors determine the relative magnitude (the number of arrows) of each specific effect (WV, WP, acid)? These effects are only qualitatively discussed in the manuscript. I think the authors should either include some calculations to show the relative importance of each effect, or they should simply omit the last 3 columns in the table.

12. Figure 1. Same as Table 1, I do not think that the authors can divide the high NOx experiments into two different periods and compare their yields with other experiments.

13. Figure 5. It would be clearer if the time-dependent growth curves for different experiments are colored. Also, the authors should include the time-dependent growth curves for the two atmospherically relevant experiments for comparison.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14467, 2008.