

Interactive comment on “Secondary organic aerosol formation from *m*-xylene, toluene, and benzene” by N. L. Ng et al.

N. L. Ng et al.

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We thank the reviewers for their comments. We have made changes to the text to address these comments. In particular, we have reorganized Sections 4.2 (Effect of oxidation rate) and 4.3 (General mechanisms of SOA formation) to further clarify the rate effect and the multiple steps in SOA formation. All changes made are minor, and they do not change the conclusion of the manuscript. Responses to specific comments are given below.

Responses to comments by reviewer 1:

1. It is my opinion that while the laboratory results are consistent with significant losses of condensable oxidation products, the absence of experimental evidence confirming this hypothesis needs to be clearly acknowledged in the manuscript. It is also unclear

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how, in general, SOA chamber data should be corrected for these losses. In addition, some comment on the impact of these losses on the reliability of currently used Odum parameters for anthropogenic and biogenic SOA precursors would be of considerable value to the modeling community.

The following sentence is added near the end of the second paragraph of Section 4.2 (Effect of oxidation rate):

"Recently, the effect of particle- and gas-phase reactions of semivolatile products on SOA formation has been examined in a modeling study by Chan et al. (2007), in which the experimental data presented in this work (among other literature data) are fitted to simple kinetic models. Given the importance of the loss of semivolatiles, these loss processes merit further investigation and experimental evidence."

The following sentence is added in Section 5 (Implication for SOA growth from aromatic hydrocarbons):

"Other than the NO_x effect, the loss of semivolatiles also affects the SOA yields measured. The depletion of semivolatiles by chemical reaction or wall loss may lead to lower SOA formation in the chambers than occurs in the atmosphere. Due to the slower oxidation rate in the classical photooxidation experiments conducted by Odum et al. (1996, 1997 a, b), it is likely that their SOA yield parameters underestimate SOA formation from aromatic hydrocarbons in the atmosphere."

2. In Figure 11, Ng compares the high NO_x m-xylene SOA yield curve with the original Odum curve reported in 1996, the latter of which has been corrected for the temperature (25°C) of the current study and the SOA density reported in this manuscript (1.48 g cm⁻³). However, both the temperature for the original Odum curve and the enthalpy of vaporization, employed to convert the SOA yields from the high temperatures in the original study to 25°C, have been omitted from the manuscript. This information needs to be included.

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For clarification, the sentence "The yield curve from Odum et al. (1996) has been adjusted based on the temperature (25°C) and SOA density (1.48 g cm⁻³) obtained in this study."

is changed to

"The aerosol yields from Odum et al. (1996) were obtained at a temperature of 35 - 40°C with an assumed SOA density of 1 g cm⁻³. In Fig. 11, the yield curve from Odum et al. (1996) has been adjusted based on the temperature (25°C) and SOA density (1.48 g cm⁻³) obtained in this study. The enthalpy of vaporization employed to convert the SOA yields from the higher temperature in Odum et al. (1996) to the lower temperature in this study is assumed to be 42 kJ mol⁻¹ (Chung and Seinfeld, 2002), which is in the range of limited experimental data (Offenberg et al., 2006; Stanier et al., 2006)."

3. Additional analyses of the time dependent growth curves in Figures 3-7 were used to identify the rate limiting steps in SOA formation for aromatic hydrocarbons..... After reading this section of the manuscript a number of times, I think I understand the argument. Perhaps some further details would make it clearer.

This paragraph has been rewritten:

"However, unlike with a-pinene ozonolysis (Ng et al., 2006), the time-dependent growth curves from experiments with different initial aromatic hydrocarbon concentrations do not overlap, and aerosol growth is not the same for a given amount of hydrocarbon reacted (Δ HC). Instead, SOA growth at a given value of Δ HC depends on the initial hydrocarbon concentration (HC₀): experiments with higher HC₀ reach a given Δ HC in a shorter time than those with smaller HC₀. At smaller HC₀, during the longer time required to reach the same Δ HC, the first generation products have more time to be oxidized to form condensable products. Therefore, the divergence in growth curves at different initial hydrocarbon concentrations indicates that even though the first step is the rate-limiting in SOA formation, subsequent oxidation steps also

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occur prior to SOA formation. As discussed in Ng et al. (2006), if subsequent oxidation steps are essentially instantaneous relative to the initial oxidation step, then SOA formation can be treated as a single step and all the growth curves will overlap. In the present study, the growth curves diverge only slightly, indicating that although the second oxidation step is not instantaneous, it is still substantially faster than the initial oxidation step. The formation of SOA by multiple oxidation steps, in which the later steps are substantially faster than the initial oxidation, is consistent with available kinetic data and current understanding of the photooxidation of aromatic hydrocarbons. In general, first-generation products of aromatic photooxidation react about an order of magnitude faster with OH than do their parent hydrocarbons (Calvert et al., 2002). For example, whereas the benzene-OH rate constant is $1.22 \times 10^{-12} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$, the rate constant of the reaction of OH with phenol, a major first-generation reaction product, is $2.7 \times 10^{-11} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2002). Our study does not exclude the possibility of formation of SOA from the condensation of first-generation products; however, it suggests that second (or further) generation products contribute significantly to SOA growth."

4. And finally, after reading the manuscript, I am not sure whether aromatic SOA forms from direct condensation of ROOH onto pre-existing aerosol or from the condensation of the oxidation products of the ROOH+OH, or perhaps from both pathways. This issue should be addressed.

The non-overlapping of the growth curves from experiments with different initial hydrocarbon concentrations implies that there are multiple steps that lead to SOA formation (Section 4.3). SOA can be formed from both the direct condensation of first generation products and from further oxidation products. This is now made clear in Section 4.3.

5. Page 4089/ Line 11. A typical aerosol wall loss rate should be included.

The following sentence is added: "Generally, the wall loss coefficients range from 10^{-4} to 10^{-2} min^{-1} ."

6. Page 4090/ Line 9. Are there any estimates of the initial HONO concentrations? Page 4089/Line 16. How does the presence of HONO affect the NO and NO₂ measurements during the irradiation experiments?

In these experiments, HONO concentration is not measured directly, but it may be detected by the NO_x monitor as NO or NO₂. As mentioned in the manuscript, hydrocarbon decay slows down after ~ 1 h, suggesting that HONO is almost completely consumed. If a large fraction of NO and NO₂ signals is from HONO, we would expect a relatively abrupt change in NO and NO₂ concentrations once HONO is depleted. Such change is not observed, indicating that it is unlikely that the presence of HONO affects the NO and NO₂ measurements significantly.

7. Page 4090/Line 26. It would be helpful if the method for estimating H₂O₂ concentrations was briefly described in the manuscript, rather than requiring the reader to refer to a reference.

The sentence "The concentration of H₂O₂ in the chamber is not measured; based on the rate of hydrocarbon decay we estimate [H₂O₂] to be ~3-5 ppm (Kroll et al., 2006)." is changed to

"The concentration of H₂O₂ in the chamber is not measured; based on the rate of hydrocarbon decay and literature values of (Sigma)H₂O₂ and kOH+H₂O₂, we estimate [H₂O₂] to be ~3-5 ppm (Kroll et al., 2006)."

8. Page 4096/Line 26. Because it plays a significant role in interpretation of the chamber data, the manuscript would be improved if a sentence or two was included describing how the work of Volkamer and Koch eliminates the possibility that nitrogen-containing ring-retaining product are responsible for the NO_x dependency.

The work of Volkamer and Koch are now discussed in more detail:

"One mechanism by which NO_x levels may affect the products formed in the oxidation of aromatic hydrocarbons is by reaction with the aromatic-OH adduct. The aromatic-

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OH adduct reacts predominately with O₂ under atmospheric conditions. Under very high levels of NO_x (ppm levels), the adduct + NO can still be neglected (Koch et al., 2006) while the adduct + NO₂ reaction increases in importance, leading to nitrogen-containing ring-retaining products such as nitrobenzene and nitrotoluene (Atkinson et al., 1989; Atkinson and Aschmann, 1994; Koch et al., 2006). The presence of a high concentration of NO_x in the chamber also has an impact on the formation yields of phenol-type compounds, possibly due to the reactions of the aromatic-OH adduct with NO and NO₂. For example, the phenol yield from benzene photooxidation starts to decrease dramatically for [NO₂] > 100 ppb (Volkamer et al., 2002). In the current work, photooxidation of m-xylene and toluene is carried out in the presence of ~500 ppb each of NO and NO₂; while for photooxidation of benzene the initial NO₂ concentration is <100 ppb. At these NO_x levels, the reaction of the aromatic-OH adduct with NO₂ is not expected to be significant (Volkamer et al., 2002; Koch et al., 2006), so such reactions cannot be responsible for the observed effect of NO_x on SOA yield."

9. Page 4099/Line 3. This paragraph is very confusing to me. It is my understanding that if the modeling study by Johnson includes photolysis of isopropyl nitrite leading to prompt OH formation, based on the rate effect, one would expect the simulation to show SOA formation in the presence of high NO values. Such SOA formation was observed by Stroud. However, apparently the Johnson modeling results showed complete suppression of the SOA, so I am confused.

The reviewer makes a good point. If the problem of Johnson's modeling is just the "missing sink of semivolatiles", then they should be able to simulate SOA formation - and they should even have a larger SOA formation if they do not include the loss of semivolatiles in the model. It is possible that the semivolatiles may be less volatile than what was assumed in the simulations of Johnson et al. (2004) (and indeed, the vapor pressures of organic nitrates are highly uncertain). This paragraph now reads as:

"Significant SOA formation from the rapid oxidation of aromatics under high (ppm) levels of NO_x has also been observed by Stroud et al. (2004), using isopropyl nitrite as

an OH source to oxidize toluene. Such results could not be reproduced in the simulations of Johnson et al. (2004), which predicted no SOA formation in the presence of such high NO_x levels, as the RO₂ + NO reaction products were found to be too volatile to partition substantially into the aerosol phase. However, the present work suggests that products of the RO₂ + NO reaction are in fact condensable, but contribute to aerosol mass only when oxidation reactions are fast, minimizing the effect of other loss processes. This underscores the need for a better understanding of the behavior of semivolatile organics in the atmosphere, in terms of both physical properties (partitioning coefficients) and chemical reactions (reactive loss processes)."

Responses to comments by reviewer 2:

1. p. 4088, line 5ff I find the formulation that the "NO_x level in chambers constantly changes", misleading. The NO_x family is used because it is a "conserved" quantity (in the atmosphere). I guess, the NO/NO₂ ratio is the important quantity that changes (even if there are some overall wall losses of NO_x). Throughout the manuscript the authors always refer correctly explicitly to NO or NO₂ where needed. So, it is sufficient to make a more precise statement of what is meant here.

In our chamber NO_x is not a conserved quantity, as a large fraction can be transformed to NO_y. However, we agree that the statement "NO_x level in chambers constantly changes" might be misleading, the sentence is changed to

"In these classical photooxidation experiments, the NO and NO₂ concentrations (hence NO/NO₂ ratio) constantly change, making it difficult to isolate the effect of NO_x on SOA formation."

2. p. 4088, line 25 and p 4090, line 22. The low NO_x regime of <1ppb. Do I understand correctly that the used air was NO_x free but the instrumentation does only allow to measure values larger than 1 ppb. Or is there a chance that there is indeed some NO_x? This should be clarified. (1 ppb NO_x can be a high NO_x regime under some instances.)

In low-NO_x experiments, no NO_x is introduced into the chambers. To clarify this, the sentence is changed to:

"In the experiments, SOA formation under two NO_x conditions is studied: (1) high-NO_x experiments in which HONO is used as the OH precursor and the NO_x level at the inception of photooxidation is ~1 ppm; and (2) low-NO_x experiments in which H₂O₂ is used as the OH precursor and no NO_x is introduced into the chambers. The background NO_x concentration is < 1 ppb, which is within the uncertainty of the NO_x monitor."

3. p. 4093, line 6-12, benzene and figure 5. There is a kink in the high NO_x benzene growth curve. This is neither mentioned in the result section nor specifically commented in the discussion section. Is the bent connected to the increasing density of data points? Please, comment in the manuscript.

Due to the rapid production of OH from HONO photolysis, the hydrocarbon decays relatively fast at the beginning of the experiments and result in faster SOA formation (hence the sparse data points). After that OH is generated mainly via NO_x/HO_x chemistry, hydrocarbon decays at a slower rate resulting in the more dense data points. The following sentence is added in Section 3.1:

"Hydrocarbon decay slows down at Δt_{HC} of approximately 90 $\mu\text{g m}^{-3}$, suggesting that HONO is almost completely consumed. After that, OH is generated mainly via NO_x/HO_x chemistry, and hydrocarbon decays at a slower rate resulting in the more closely spaced data points. The slower hydrocarbon oxidation rate after the consumption of HONO may affect the kinetics of SOA growth and contribute to the slight change in the shape of the growth curves."

4. p.4099f, line 16ff My idea would be that here the smaller source of non-volatiles at same sink - wall loss -, suppresses the formation of nuclei or their growth to critical sizes. If this is the case seed aerosols should suppress some of the effect. Do you have "classical" seeded experiments/results, which could help here.

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In all experiments presented in this manuscript, seed particles are introduced into the chambers and so aerosol growth proceeds through condensation on the seed particles. In a recent paper by Kroll et al. (2007), it was found that SOA yields from aromatic photooxidation are higher in the presence of seed particles than in nucleation experiments. The loss of semivolatiles has been proposed as an explanation for the observed yield difference. This has been discussed in the manuscript (page 4099, line 17).

5. p.4102, line 7f, Only the growth curves at the largest concentrations deviate, the systems with smaller initial concentration look pretty similar. Is there a threshold concentration or may be another parameter, which induces this type of deviation?

As seen in Figure 6 (and to a lesser extent, Figs 3 and 7) growth curves at low concentrations deviate as well. We believe this deviation occurs regardless of the initial hydrocarbon concentration, and is a result of the multiple steps in SOA formation, in which the latter steps are substantially faster than the initial oxidation.

6. p.4090, line 16. I hope, that 1 ppm is the upper range of your NO_x monitor and not the detection limit?!

1 ppm is the upper detection limit of the NO_x monitor. To clarify, the sentence is changed to:

"Additional NO from a 500 ppm gas cylinder (Scott Marrin, Inc.) is introduced into the chamber after the addition of HONO to achieve a total NO_x level in the chamber of about 1 ppm (upper limit of the NO_x monitor)."

Responses to comments by reviewer 3:

1. For the classic photooxidation experiments (Figure 2, p4118), several questions arise, a) Why the concentration of ozone formed in this experiment was so high, while no ozone was detected in other experiments?

In classical photooxidation experiments, ozone is formed as a result of the photolysis of NO₂ (the concentration profile of NO₂ is not shown in Figure 2). As noted in the

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manuscript (Sections 3.1 and 3.2), under low-NO_x conditions, ozone formation of ~10–15 ppb is observed, possibly owing to residual material released from the chamber walls. Under high- NO_x conditions, ozone formation is suppressed because of the high concentrations of NO.

b) Considering the onset of the experiment in figure 2a and the experiment at ~1200 min after turning on the blacklight in figure 2b, both concentrations of NO was almost the same (~100ppb) and the concentration of m-xylene in figure 2b was higher than that in figure 2a. Why there was no SOA formation after t=1200min in figure 2b? The OH was not depleted at t=1200 min, since the authors speculated that the OH was likely from the photolysis of HONO formed from heterogeneous reaction of NO₂ on the chamber wall (p 4092) and NO₂ concentration in experiment shown in figure 2b should be high due to the reaction between peroxy and NO.

In Figure 2a, aerosol growth does not start immediately; only when NO concentration approaches zero does SOA growth begins. As [NO] approaches zero, the RO₂ + HO₂ reaction can compete with RO₂ + NO and form products that more readily partition into the aerosol phase (Please refer to the manuscript page 4097, line 29). In Figure 2b, NO concentration is ~100 ppb at t = 1200 min. With such a high NO concentration, RO₂ reacts predominately with NO and results in the formation of relatively volatile products.

2. Wall loss was an important factor which affected the “induction period” in experiments without seed particles and thus the SOA formation. An estimation of wall loss should be given.

The loss of semivolatiles (to the chamber walls, and/or through further reactions in the gas phase to form volatile products) has been proposed as one of the mechanisms for the higher SOA yields observed in the presence of seed aerosols as compared to nucleation experiments (Kroll et al., 2007), as well as the effect of oxidation on SOA formation (this manuscript). Recently, a kinetic modeling study by Chan et al. (2007) has examined the effect of particle- and gas-phase reactions of semivolatile products

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on SOA formation, in which the experimental data presented in this manuscript are fitted to simple kinetic models. Instead of presenting the details in this manuscript, this reference has been added to the manuscript (Section 4.2):

"Recently, the effect of particle- and gas-phase reactions of semivolatile products on SOA formation has been examined in a modeling study by Chan et al. (2007), in which the experimental data presented in this work (among other literature data) are fitted to simple kinetic models."

3. A recent experimental paper on the product distribution of the OH-initiated oxidation of m-xylene needs to be discussed in the context of the relevance to SOA formation (J. Zhao, J. Photoch. Photobio. A 176, 199-207 (2005)).

We acknowledge that the paper mentioned also addresses the reaction mechanism of m-xylene in the presence of NO_x. This reference has been included in the manuscript in Section 4.1, "Theoretical studies have shown that the peroxy radicals preferentially cyclize to form bicyclic radicals, which then react with O₂ to form bicyclic peroxy radicals (Andino et al., 1996; Lay et al., 1996; Suh et al., 2003; Fan et al., 2006), even in the presence of ppm levels of NO (Zhao et al., 2005; Fan et al., 2006). Because of the high energy barrier, the isomerization of bicyclic radicals to form epoxide radicals is unlikely for toluene; only a small fraction of epoxy carbonyls are observed in m-xylene photooxidation, suggesting that the epoxide radical channel is not important either (Suh et al., 2003; Zhao et al., 2005)."

4. The author proposed a "rate effect" mechanism by assuming that the SOA formation was driven by multiple oxidation steps, which the later steps were substantially faster than the initial rate-limiting step. This argument was not very well addressed; the authors need to clarify their multiple oxidation mechanism in a better way (p 4102).

It appears that there is a misunderstanding. The "rate effect" (Section 4.2) refers to the observation that SOA yields are higher when the oxidation rate of the parent hydrocarbon is faster. This "rate effect" could arise from the loss of semivolatile through pro-

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cesses not forming SOA. In section 4.3, based on the observation that growth curves from experiments with different initial hydrocarbon concentrations do not overlap, we propose that there are multiple steps in SOA formation, in which the later steps are substantially faster than the initial oxidation steps. This is different from the "rate effect" discussed in Section 4.2.

To avoid confusion, we have reorganized the paragraph regarding the multiple oxidation steps (Section 4.3). Please refer to the response to Reviewer 1, comment #3.

5. A simplified SOA formation mechanism is shown in figure 10. However, the authors ignored one of the most important reaction steps which involved reaction between the primary peroxy radical and NO under elevated NO concentration conditions. The authors need to address the criteria for choosing the reaction sequences.

According to Zhao et al. (2005) and Fan et al. (2006), the rate of isomerization of primary peroxy radicals to form bicyclic radicals is about 2-3 orders of magnitude faster than its reaction with NO, even in the presence of ppm levels of NO. Thus in the manuscript it is stated that "Theoretical studies have shown that the peroxy radicals preferentially cyclize to form bicyclic radicals, which then react with O₂ to form bicyclic peroxy radicals (Andino et al., 1996; Lay et al., 1996; Suh et al., 2003; Fan et al., 2006)." To further clarify, this sentence is changed to

"Theoretical studies have shown that the peroxy radicals preferentially cyclize to form bicyclic radicals, which then react with O₂ to form bicyclic peroxy radicals (Andino et al., 1996; Lay et al., 1996; Suh et al., 2003; Fan et al., 2006), even in the presence of ppm levels of NO (Zhao et al., 2005; Fan et al., 2006)."

6. During the course of the experiments, a temperature increase of 5 K inside the chamber was found. Increasing temperature might lead to the change of volatility distribution, which further affected the SOA formation. The effect of temperature elevation needs to be addressed.

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While the temperature inside the chamber increases by $\sim 5^{\circ}\text{C}$ over the course the experiments, the instruments are located outside the chamber enclosure and are at the temperature of the surrounding room, in which the temperature does not fluctuate significantly. This is clarified in the experimental section:

"The initial temperature of the chamber is $\sim 20^{\circ}\text{C}$. Heating from the lights leads to a temperature increase of approximately 5°C inside the chamber over the course of the experiment. The analytical instruments are located outside the chamber enclosure and are at the temperature of the surrounding room ($\sim 20\text{--}22^{\circ}\text{C}$). The air may cool slightly as it is sampled from the chamber into the instruments, and the measured aerosol likely corresponds to the gas-particle partitioning at the temperature of the instruments rather than the chamber enclosure. Such small temperature differences are unlikely to affect results significantly."

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4085, 2007.

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