

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

Anonymous Referee #3

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In this paper the authors have re-examined the role of aromatic hydrocarbons in secondary organic aerosol (SOA) formation by performing environmental chamber study using *m*-xylene, toluene and benzene as sample hydrocarbons. The main goals of the study are to investigate the NO_x dependences on the SOA formation and the acidity effect on the SOA growth. The authors found under even high NO_x conditions, SOA formation still form, in contrast to previous chamber studies which showed no SOA formation under high NO_x conditions. This finding may have important implications since both aromatic hydrocarbons and NO_x level are high in the urban area. The results also indicated that the aerosol yields under low NO_x conditions are more favorable than under high NO_x conditions. They interpreted this NO_x dependence as the differences of peroxy radical chemistry under low and high NO_x conditions, since the peroxy

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+ NO reaction is dominant under high NO_x conditions while the peroxy + HO₂ reaction is prevalent under low NO_x conditions. In addition, the products from peroxy + HO₂ possess lower volatility than those from peroxy + NO, which explains the different SOA yields under low and high NO_x conditions. Another conclusion drawn from the study is that no evidences of acid-catalyzed reactions have been found to contribute to SOA formation. The authors present a nice work on the SOA formation from aromatic hydrocarbons. There are a number of issues that should be addressed before the publication of this work. (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? 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. (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. (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)). (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). (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

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NO concentration conditions. The authors need to address the criteria for choosing the reaction sequences. (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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