Atmos. Chem. Phys. Discuss., 7, S1226–S1232, 2007
www.atmos-chem-phys-discuss.net/7/S1226/2007/

Atmospheric
Chemistry
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Discussions

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

Anonymous Referee #1

Received and published: 17 April 2007

General Comments

Over the past two decades, laboratory smog chamber studies have been carried out to develop the information needed to construct SOA chemistry models for atmospherically relevant aromatic hydrocarbons. For each SOA precursor, the aromatic hydrocarbon is irradiated in the presence of NOX for a series of reactant concentrations. The amounts of SOA produced and hydrocarbon reacted at the end point of each experiment are used to determine (1) the yields of condensable oxidation products and (2) equilibrium coefficients for their partitioning between the gas and aerosol phases, both of which are required for the two-product SOA chemistry model developed by Odum and co-workers at Caltech. Over the past decade, the Odum model has served as the SOA chemistry model in many assessments of the contribution of SOA to ambient OC con-

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centrations. Recently, researchers have turned their attention to the challenging task of developing more advanced SOA chemistry models by modifying explicit gas phase chemistry mechanisms such as the Caltech Atmospheric Chemistry Mechanism and the Master Chemical Mechanism to include partitioning of selected oxidation products. It is likely, however, that in the short term the Odum model or a variation of it will still play a significant role in assessing contributions of the major sources of SOA to ambient OC concentrations. If the Odum model is to be utilized, it must be updated to take into account any impacts of NOX and aerosol acidity on SOA formation.

The research program carried out by Ng and co-workers consisted of conducting four types of experiments to investigate the roles of NOX and aerosol acidity in SOA formation from aromatic hydrocarbons. A few HC/NOX irradiations, which are referred to in the manuscript as classical photooxidation experiments, were carried out. In addition, a series of HC/NOX irradiations were conducted with HONO added as a OH radical source. These experiments are referred to as high NOX experiments. The third series of experiments, identified as low NOX experiments, consisted of irradiating hydrocarbons in the presence of hydrogen peroxide (H2O2), which generates OH radicals through its photolysis. The final type of experiment consisted of conducting both high and low NOX experiments in the presence of acidified seed aerosol. In this research program, Ng uses high NOX experiments to investigate SOA formation involving RO2+NO reactions, while SOA formation from RO2 +HO2 reactions is the focus of low NOX experiments.

Figure 2a in the manuscript shows the reaction time profile for a classical photooxidation experiment, conducted during the current study, with reactant concentrations of 102 ppb m-xylene and 123 ppb NOX. In this experiment, SOA forms only after all the NO has been consumed. Figure 2b displays the time profile for another classical photooxidation experiment with 95 ppb m-xylene, with the NOX level raised to 943 ppb. The additional NOX reduces significantly the reactivity of the irradiated mixture as demonstrated by the 100 ppb of NO remaining after nearly 1400 minutes, with negligi-

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ble amounts of O3 formed and no SOA detected. Finally, Figure 1 shows the results of a high NOX experiment with 89 ppb m-xylene and 943 ppb NOX, but with HONO added to the mixture. The high NOX experiment shows prompt formation of SOA.

By comparing the results of these three experiments Ng was able to gain considerable insight into the impact of NOX on SOA formation from m-xylene. Ng addressed the question of why SOA forms in the presence of NO in the high NOX experiment, presumably through RO2+NO reactions, but not in its presence in the classical photooxidation experiments. Ng argues the difference between high NOX and classical photooxidation results can be explained by a rate effect. The presence of HONO results in much higher OH radical concentrations in the high NOX experiment than those occurring in the classical photooxidation experiments where the initial OH concentrations are thought to be the result of wall reactions of NOX compounds. The higher OH concentrations lead to enhanced formation rates of the condensable oxidation products forming SOA. Ng then goes on to assume there are significant losses of condensable products in the smog chamber preventing SOA formation, possibly due to wall loss, photolysis, and fast reactions that form volatile compounds. Based on this hypothesis, Ng concludes that, in the classical photooxidation experiments, due to the low OH concentrations, the combination of slow formation rates of condensable oxidation products and their significant removal rates leads to very low levels SOA observed, if SOA is observed at all. On the other hand, the presence of HONO in the high NOX experiments results in rapid formation of condensable compounds so that, even in the presence of considerable losses, significant levels of condensable products remain to form SOA. 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 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.

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SOA yield data for the m-xylene, toluene and benzene high NOX experiments, that were conducted over a range of initial hydrocarbon concentrations, are summarized in Table 2-4 and are displayed in a series of time dependent growth curves in Figures 3-5, where the SOA formed is plotted against the hydrocarbon reacted. Data for m-xylene and toluene, used to construct the yields curves displayed in Figure 8, were employed to calculate the new high NOX 2-product Odum parameters tabulated in Table 6. In Figure 11, Ng compares the high NOX 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 (1.48 g cm-3) reported in this manuscript. 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.

The time profile for the classical photooxidation experiment in Figure 2a shows SOA from m-xylene can also form in the absence of NO. While the chemistry of RO2 in the absence of NO is not well understood, Ng shows, by comparing reactions rates of the RO2+HO2 reaction with those of RO2+RO2 reaction, that the organic peroxide ROOH formed from the RO2+HO2 reaction could be a significant contributor to SOA once the NO has been consumed. Clearly, this hypothesis needs experimental confirmation. To further investigate possible SOA-forming organic peroxide reactions, Ng carried out a series of low NOX experiments for the three aromatic hydrocarbons. The results are displayed in the form of time dependent growth curves shown in Figures 5-7. In these experiments, where no NOX has been added, ROOH is likely to form as soon as irradiation begins. Inspection of the low NOX growth curves shows they are all straight lines which, according to Ng, is consistent with constant yields of nonvolatile SOA. The low NOX SOA yields of 36%, 30%, and 37% for m-xylene, toluene and benzene, respectively, are presented, along with the two-product model high NOX yields, in Table 6. These values suggest the RO2+HO2 reaction could be a significant SOA pathway and needs to included in SOA chemistry models along with the contributions initiated by RO2+NO reactions.

To assess the impact of acidity on SOA formation, Ng compared time dependent growth curves, displayed in Figure 9, for the high and low NOX experiments for toluene and m-xylene with neutral and acidic (pH = -1.7 calculated using the Aerosol Inorganic Model II (AIM)) seed aerosol for 5% RH. Ng observed no evidence of acidity enhancing SOA formation for either of these two hydrocarbons. However, for completeness, as noted by Ng ,further experiments should be conducted at more atmospherically relevant RHs.

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. Based the observation that once the hydrocarbon had completely reacted there is no further SOA formed, Ng concluded the first oxidation step in the mechanism controls the SOA formation rate. However, Ng also observed the time dependent growth curves for different initial hydrocarbon concentrations did not overlap and the amount of SOA formed was not the same for a given amount of hydrocarbon reacted. In particular, for experiments at higher initial hydrocarbon concentrations, the time taken to react a given amount of hydrocarbon was less than for those experiments starting with a lower hydrocarbon concentration, thus leaving more time in the latter case for the first generation products to form SOA. Ng argues this divergence in growth rates implies that, even though the first oxidation step is the limiting step for SOA formation, there are additional oxidation steps occurring before SOA is formed. However, because the differences in the growth curves are small at different initial hydrocarbon concentrations, these additional oxidation steps, that still may affect the kinetics somewhat, are substantially faster than the rate limiting first oxidation step. Ng concludes her discussion of rate controlling steps by noting that formation of SOA through a multi-step mechanism with the later steps occurring substantially faster than the initial oxidation step is consistent with our current understanding of photooxidation of aromatic compounds. 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.

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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.

Summary Statement

The results of this novel laboratory study to assess the roles of NOX and aerosol acidity in SOA formed from photooxidations of toluene, m-xylene and benzene have provided some of the critical information needed to predict the contributions of these high volume aromatic compounds to ambient OC concentrations. The experiments have been carefully planned and carried out, and the resulting the data is of high quality. The interpretation of the laboratory data appears to be sound and, with the exceptions noted above, is clearly presented. While the hypotheses of rapid loss of condensable products and the formation of organic peroxides still await experimental confirmation, I believe the atmospheric chemistry as well as the regulatory science communities will view this research as an important step in identifying the key chemical pathways that contribute significantly to the formation of aromatic SOA.

Minor Comments

Experimental Section

Page 4088/ Line 11. A typical aerosol wall loss rate should be included.

Page 4089/ 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 ?

Page 4089/ 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.

Discussion

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 NOX dependency.

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.

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