Atmos. Chem. Phys. Discuss., 8, S7549–S7553, 2008
www.atmos-chem-phys-discuss.net/8/S7549/2008/

Atmospheric
Chemistry
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Discussions

Interactive comment on “Temperature dependence of yields of secondary organic aerosols from the ozonolysis of α-pinene and limonene” *by* H. Saathoff et al.

Anonymous Referee #2

Received and published: 26 September 2008

In this work, the authors conduct experiments examining the SOA yield from the ozonolysis of α-pinene and limonene across a wide range of temperatures. The data are analyzed with a model and the temperature dependence of the vapor-pressure, mass yield, and equilibrium partitioning coefficients for two model compounds are parameterized. These data are very useful for SOA modeling studies especially considering the current sparse data detailing the temperature-dependence of SOA yields. The paper is generally well written, though a little long, and the material is appropriate for publication in ACP. The experiments appear to be carefully conducted; however, I have some concerns about the treatment of the wall loss of semivolatile species that I would like to see addressed before publication.

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Primary General Comments

Through the paper the authors highlight the importance of evaluating the loss of semi-volatile species to the walls during the course of their experiment. They explain that the two-product model is inadequate for interpretation of their data because of this loss and a model was required to evaluate the data. They show that the correction for gas phase wall loss is large and appears to dominate the data on a mass basis, particularly at higher temperatures. However, the authors have treated the wall loss of semi-volatile species as irreversible. I question the validity of this approach and would like to see some justification for this treatment. It seems counterintuitive that organic gas phase species would establish equilibrium with the suspended particle phase but not with the walls. Have the authors conducted experiments showing that volatilization of organic material from the walls is unimportant? How would the temperature dependences of the SOA yields change if the loss of organics to the walls were reversible instead of irreversible?

Additional General Comments

In general, I think the paper is longer than necessary, though I do not have specific suggestions on where to shorten it.

Stanier et al. (2007) have also examined the temperature-dependence of SOA from the ozonolysis of α-pinene (Stanier et al., 2007). Please including this work in the discussion of literature results where appropriate.

Additional Specific Comments

Page 15600, line 1. Please provide the concentration of ozone entering the chamber or the information necessary to determine this. 3% ozone is an extremely high concentration and at these levels reactions occurring with slow rates, for instance the particle phase ozonolysis reactions, may become important (Bailey, 1982b; Bailey, 1982a). This is potentially important later in the experiment when ozone levels in the chamber are replenished while aerosol is present in the chamber. Can the authors comment on such a possibility?

Page15600, line22. It is confusing to have tables labeled as 1a and A1 both in the body of the paper. I suggest relabeling the tables in a more conventional, consecutive fashion.

Tables 1a and 1b. The authors should think about combining these 2 tables into 1. The first three columns are identical and it would make interpretation easier. The same applies to Table 2a and 2b.

Pages 15601-15602. Some of the aerosol instrumentation lies outside the temperature-controlled chamber. Can the authors comment on the residence time of the particles in lines running to instrumentation that is not temperature controlled? Possible evaporation of particles in these lines could effect the number concentration, mass concentration, density determination, etc.

Page 15605, lines 19-25. Please clarify the statement: “it proved impossible to conduct an analogous analysis within the framework of the K- α approach“. Many of the parameters derived from the model and presented in the paper are presented in the K-α framework.

Pages 15612-15613. It appears the authors have conducted a sensitivity study to evaluate the effect of certain parameters (e.g., MW, density, surface tension) on the final simulation. A table of these results would help organize this information for the reader and clarify the relative importance of the parameters on the results.

Page 15615, 15616. It is very difficult to directly compare α and K values from different experiments for a number of reasons, as the authors themselves point out (e.g., p15598). Therefore, I suggest removing comparisons of α and K to literature results.

Page 15625 Line 23-25. Please clarify and revise the statement “SOA yield from α 8211;pinene, which is a poor SOA precursor near room temperature“. I object to this statement as it is currently written. α-pinene yields in the literature, coupled with its high emission rate relative to other mono- and sesquiterpenes suggest it is an important

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contributor to SOA on a global scale even at room temperature (Griffin et al., 1999; Kanakidou et al., 2005).

Figure 7. It is very difficult to distinguish between the shades of blue and green used in the color coding, particularly when printed. Please change the color scheme.

Page 15619. The authors should comment more on the role of RH. Is the RH dependence observed at 253 K significant given the experimental uncertainty? It is somewhat strange that the 253 K data set is the only one that displays any RH dependence. If absolute water vapor concentration were the cause, as suggested at line 27, I would expect the 303 K data to also display an RH dependence.

Page 15621 and Figures 10a and b. There is no evidence for oxidation of the second limonene double bond in these figures. The shape of the time-dependent yield curves for limonene ozonolysis is distinctly different than that observed by both Zang et al. (2006) and Ng et al. (2006) (Ng et al., 2006; Zhang et al., 2006). For example, in Figure 10a and b, SOA formation appears to stop after limonene is consumed, in contrast to the behavior observed in Fig. 2 of Ng et al. (2006) and Fig. 8 of and Zhang et al. (2006). The authors should comment on this discrepancy.

References

Griffin, R. J., Cocker, D. R., Seinfeld, J. H. and Dabdub, D.: Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, Geophys. Res. Lett., 26, 2721-2724, 1999.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., VanDingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G. and Wilson, J.: Organic aerosol and global climate modelling: A review, Atmos. Chem. Phys., 5, 1053-1123, 2005.

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Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R. C., Seinfeld, J. H., Lee, A. and Goldstein, A. H.: Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, Environmental Science Technology, 40, 2283-2297, 2006.

Stanier, C. O., Pathak, R. K. and Pandis, S. N.: Measurements of the volatility of aersols from a-pinene ozonolysis, Environ. Sci. Technol., 41, 2756-2763, 2007.

Zhang, J., Huf-Hartz, K. E., Pandis, S. N. and Donahue, N. M.: Secondary organic aerosol formation from limonene ozonolysis: Homogeneous and heterogeneous influences as a function of NOx, J. Phys. Chem. A, 110, 11053-11063, 2006.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15595, 2008.

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