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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.

H. Saathoff et al.

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The authors would like to thank the referees for their thoughtful annotations. Please find below our answers to the individual comments.

Referee 1

RC 1. "The authors need to elaborate how they determined the wall loss rate coefficient of the two effective SOA proxies in the gas and particle phase."

AC 1. The wall loss coefficients of the two compounds were treated as adjustable parameters in fitting the model to the measured particle masses, number concentrations, and size distributions. It turned out that the wall loss rate coefficient for product

2 could be determined quite well. Overall, the wall loss rate coefficient of product 2 had a smaller effect on the modelling results Nevertheless, this parameter could also be successfully constrained ,due to its significant influence on the evaporation rate of the smaller particles. To justify our assumption that the loss to the chamber walls is effectively irreversible we will add the following sentences to section 4.1.1.:

"Please note, that for both cases illustrated in Fig. 2 the total of condensable gaseous species lost to the chamber wall remains well below the equivalent of one monolayer (estimated to about 200 μg m-3 based on the molecular size parameters reported by Bilde and Pandis (2001) and assuming a perfectly flat wall surface). The same applies to all experiments considered in this paper. Furthermore, modelling experiments SOA05-1 and SOA05-13 conducted at 303 K where the time evolutions of size distribution and mass concentration have been monitored for more than 17 hours after the last injection of alpha-pinene the observations could be consistently reproduced allowing complete evaporation of product 2 from the particle phase. Thus, the assumption of irreversible wall losses appears to be reasonable."

And:

"In our case, the detailed process model analysis of SOA experiments, although much more complex due to the simultaneous consideration of trace gas and particle wall loss effects on size distribution as well as mass and number concentration, allows accounting for all relevant loss processes without suffering from the limitations mentioned above."

RC 2. "Do the authors fit the K,i and alpha,i values or po,I and alpha,i values with the experimental data? Is a constant <MWo> value assumed for calculating the K values using Eqn. 3 in ozonolysis of alpha-pinene and limonene"

AC 2. The COSIMA model fits the vapour pressures and alpha values to the experimental data. The partitioning coefficients are calculated from p1 and p2 in the limit of large Mo where <MWo> approaches a constant value. To make this point clear we will add the following sentences to Section 4.1.3.:

"Please note that K1 and K2, calculated from p1 and p2 in the limit of large Mo where <MWo> approaches a constant value, are provided here in order to facilitate the comparison of our results with literature data. Since the concept of partitioning coefficients is only meaningful for equilibrated systems it is not used within the framework of the COSIMA model."

RC 3. "In section 4.2.2, for the ozonolysis of limonene, the same values as for the experiments with alpha-pinene are used for surface tension, diffusion coefficients and molecular mass of the two effective SOA proxies. Is there any reason for this assumption? Are the SOA products formed from the ozonolysis of limonene similar to those formed from the ozonolysis of alpha-pinene? The same question applies to the effective evaporation enthalpy of the volatile SOA product (page 15624, line 11)."

AC 3. Since the products reported in the literature for the limonene ozonolysis (Glasius et al., 2000; Larsen et al., 2001; Leungsakul et al., 2005; Northcross and Jang, 2007; Walser et al., 2008) are quite similar to those reported for alpha-pinene it is reasonable for us to use also similar values for surface tension, diffusion coefficients and molecular mass for the two effective SOA proxies. To make this point clear we will add the following sentences to section 4.2.2.:

"In the model analysis the same values as for the experiments with alpha-pinene were used for molecular masses, surface tensions, and diffusion coefficients of the two components. This appears reasonable since MW1=186 g/mol and MW2=168 g/mol also correspond to typical monomeric oxidation products of limonene such as limonic acid or limononaldehyde (Glasius et al., 2000; Leungsakul et al., 2005; Walser et al., 2008). Furthermore, the molecular subgroups that could be considered as intermolecular interaction sites within the framework of a group contribution approach are similar for the ozonolysis product species of both terpenes."

The effective evaporation enthalpies for the limonene SOA proxies were determined

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independently from the experimental data but on the basis of the model assumptions made for the limonene SOA.

RC 4. "In section 4.1.5 (Page 15619), "During this work a substantial impact of the humidity on the SOA yields from alpha-pinene ozonolysis was only observed for the lowest temperatures investigated. The SOA yields for experiments under very dry conditions at 253 K are significantly lower than corresponding humid experiments (Fig. 7)." As shown in Figure 7, the SOA yields under dry and humid conditions at 253K (blue solid and open square) and at 243K (blue solid and open cycle) lie within the uncertainty of the data. The data do not appear to be able to clearly demonstrate the effect of RH on SOA yield of ozonolysis of alpha-pinene at low temperature."

AC 4. Indeed the influence of relative humidity or absolute water concentration on the yield is not clearly demonstrated in the data shown. Therefore we will change the first sentence in section 4.1.5. to:

"From this work a significant impact of humidity on the SOA yields from alpha-pinene ozonolysis, if present at all, can only be taken into consideration for the lowest temperatures investigated."

RC 5. "All the authors have done is to state that the data show. Without a fundamental mechanistic explanation of the differences in these experiments, the current data are of little use. These experiments were presumably carried out to provide data that can be used to evaluate ones' fundamental understanding of the RH effect. Lack of this is the greatest weakness of the present paper."

AC 5. A possible mechanistic explanation of the influence of water on SOA formation will be given in the companion paper by Tillmann et al. (2008b) in this journal.

RC 6. "As shown in Figures 2b and 10b, the amount of more volatile product (Product 2) looks always larger than that of the less volatile product (Product 1) at low temperature. Also, the amount of more volatile product is always larger than that of less volatile

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product, even at low organic mass loading. On the other hand, the amount of more volatile product always smaller than that of the less volatile product at high temperature (Figure 2a and 10a). This is opposite to what one would expect. Do the authors have any explanation?"

AC 6. As expected, at low temperatures a much larger portion of product 2 partitions into the condensed phase. Furthermore, the behaviour of the particle composition presented in the middle panels of figures 2 and 10 shows that alpha 2 exhibits a much larger variation with temperature compared to alpha 1. A mechanistic interpretation of the temperature dependence of alpha 1 and alpha 2 is beyond the scope of this paper as stated in Section 3, page 15604, lines 23-24.

RC 7. "Page 15607, line 7, it is stated that "At and above 303 K the initial growth rate of the SOA mass is comparable to the decay rate of the alpha-pinene mass. Hence, the ozonolysis is the rate limiting step for the SOA formation under these conditions. With decreasing temperature, however, the initial rate of SOA mass formation gradually slows down compared to the decay of the precursor mass concentration. At 243K the degradation of alpha-pinene proceeds approximately two times faster than the creation of condensed material." This observation is not clearly evident in Figure 2."

AC 7. The conclusion that SOA formation is delayed at low temperature, which may not be evident by visually comparing the decay of the terpene with the rise of the SOA mass in Figure 2b, is however strongly supported by the model fit to the experimental data. We take this as evidence that kinetics may play an important role e.g. if one uses simultaneous particle mass and terpene measurements to determine yield data on-line.

RC 8. "Figures 8 and 15 show the temperature dependence of SOA yields from alpha-pinene ozonolysis and limonene ozonolysis for organic mass loading, Mo at 10 μg m-3, respectively. However, no SOA yield data below Mo= 10 μg m-3 are listed in Tables 1 and 2. Below Mo= 10 μg m-3 a few SOA yield data are shown in Figure 7 (alpha-pinene) and no data point are shown in Figure 14 (limonene)."

AC 8. As stated in line 11 of page 15619 the parameterisation has been used to construct a temperature dependent plot (Figure 8) for a constant organic aerosol mass of 10 μg m-3. The data given in Tables A1 A2 and shown in Figures 7 14 are only those obtained for relatively stable conditions after practically complete oxidation of the terpene added in the previous addition step. The model analysis is based on more data points and includes data for SOA masses starting at typically 3-4 μg m-3. Therefore we will add the following sentences to the end of section 4.1.4.:

"Please note that the model analysis is based on more data points than those listed in Tables A1 A2 or shown in Figures 7 14. Typically all data points measured at > 4 μg m-3 aerosol mass were successfully fitted by the model. Therefore the parameterisation given should be valid down to 4 μg m-3 of organic aerosol mass."

RC 9. "Page 15650, Figure 6a, alpha,1 and alpha,2 is missing in the figure. Page 15661, Figure 13a, alpha,1 and alpha,2 is missing in the figure."

AC 9. We don’t see alpha 1 or alpha 2 missing in Figures 6a and 13a.

AC 10. All comments on spelling or repetitions are appreciated, and the manuscript will be changed accordingly.

Referee 2

RC 1. "Through the paper the authors highlight the importance of evaluating the loss of semivolatile 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

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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?"

AC 1. We refer to the justification of our conclusion that the losses to the chamber walls are effectively irreversible which was given to Referee 1. Especially the experiments conducted over more than 24 hours are consistent with this conclusion. Note that the wall coverage remains well below the equivalent of one monolayer, even if the wall loss of the semivolatile material were 100

RC 2. "Stanier et al. (2007) have also examined the temperature-dependence of SOA from the ozonolysis of alpha-pinene (Stanier et al., 2007). Please including this work in the discussion of literature results where appropriate."

AC 2. The paper (Stanier et al., 2007) will be included in the introduction and section 4.1.4. of the manuscript.

RC 3. "Page 15600, line 1. Please provide the concentration of ozone entering the chamber or the information necessary to determine this. 3

AC 3. This question addresses a general problem when adding reactants to a simulation chamber. If a significant increase in concentration of a reactive compound needs to be achieved within a limited time high concentration levels at the inlet are hard to avoid. Note, however, that high ozone concentrations only occur in a "plume" at the inlet which contains a negligibly small mass fraction of the chamber aerosol. Note furthermore that the mixing fan provides homogeneous mixing within 1-3 minutes and hence speeds up the dilution of high local ozone concentration levels. The ozone produced in concentrations of about 3 percent in the ozone generator was typically diluted to about 1 percent in a 1 litre glass bulb from which the ozone was added into the AIDA chamber with a stream of synthetic air of 5 litres per minute. The highest concentra-

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tions were added before the terpene or SOA were present. We think the fast mixing in the chamber volume limited the influence e.g. of concentration gradients or of particle phase ozonolysis reactions. Particle phase characterisation e.g. with AMS or VTDMA did not show a significant influence of subsequent ozone additions. The concentration information will be added to the experimental section:

"Ozone was generated by a silent discharge generator (Semozon 030.2, Sorbios) in mixing ratios of about 3 percent in pure oxygen and added to the chamber either directly or more typically after dilution to about 1

RC 4. "Page15600, line22. It is confusing to have tables labelled as 1a and A1 both in the body of the paper. I suggest relabeling the tables in a more conventional, consecutive fashion."

AC 4. The numbering of tables is indeed confusing. The journal requires to use A1, A2, etc., where the capital A stands for "Appendix". We will combine the tables 1a with 1b into table 1 as well as tables 2a with 2b into table 2 to solve the problem.

RC 5. "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."

AC 5. The authors will combine the Tables as suggested; see our response to the previous comment.

RC 6. "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."

AC 6. The sampling lines to the instrumentation outside the thermostated part of the AIDA have an inner diameter of 4 mm. With the sampling flows of the instruments and lengths of the sampling lines the times that particles are exposed to room temperature before entering the CPCs and SMPS instruments are about 2 seconds. Comparison of measurements with the SMPS outside the temperature controlled area and the DMPS system inside the temperature controlled area showed differences much less than e.g. the stated uncertainties in particle volume even for the lowest temperatures. Therefore we do not have an indication that there was a substantial influence of sampling position on particle volume and number concentration for these instruments. The AMS was connected directly to the thermostated housing and the residence time of particle in not temperature controlled lines was less than 1 second. Therefore evaporation of particles should not have a significant influence on the density determinations. For the VTDMA measurements the particles were equilibrated at 23°C before analysis. Therefore these results are independent of the temperature difference between the simulation chamber and the outside. We will add the following sentences to the experimental section of the manuscript:

"The typical residence time of aerosol particles in the room temperature sections of the sampling lines for measurements with the CPC's and the SMPS is 2 seconds. Differences between measurements with the SMPS (with DMA particle selection at room temperature) and the DMPS (with DMA particle selection at aerosol chamber temperature) were within measurement uncertainties even for the lowest temperatures in the aerosol chamber. Nevertheless, the SMPS results were normalised to the DMPS data to correct for potential particle losses due to evaporation."

RC 7. "Page 15605, lines 19-25. Please clarify the statement: "it proved impossible to conduct an analogous analysis within the framework of the K-alpha approach". Many of the parameters derived from the model and presented in the paper are presented in the K-alpha framework."

AC 7. Some of the problems associated with wall loss corrections to measured SOA yield data within the framework of the K-alpha approach are discussed in Section 4.1.1 and there is a respective reference in line 23 of page 15605. Furthermore, accounting for Kelvin effect and non-equilibrium behaviour turned out to be indispensable in the model analysis (see Section 3, page 15605, lines 1-8). Equilibrium partitioning coefficients (derived from fitted vapour pressures) and mass stoichiometric yield coefficients are presented to facilitate the comparison of our results with literature data.

RC 8. "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."

AC 8. As outlined in Sections 4.1.2, 4.1.3, 4.2.1, and 4.2.2, experimentally determined values were used for the SOA densities, while the molar weights of the product proxies were chosen to correspond to typical low and semi volatile oxidation products of alpha-pinene and limonene, respectively. Therefore, no attempt was made to investigate the sensitivity of the simulation results with respect to variations of these parameters. The effect of varying yield factors, vapour pressures, surface tensions, effective accommodation coefficients, and wall loss rate constants was analysed extensively, but we did not attempt to conduct a fully comprehensive sensitivity study. The effect of vapour pressures, surface tensions and the influence of the Kelvin effect on the time evolutions of modelled size distributions, mass and number concentrations will be discussed in a forthcoming paper (Naumann, 2008).

RC 9. "Page 15615, 15616. It is very difficult to directly compare 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 alpha and K to literature results."

AC 9. We want to mention at least a limited number of references to give the reader a little orientation about the range of values available. For the alpha values the comparison is generally not so problematic but indeed the K values depend on experimental conditions.

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RC 10. "Page 15625 Line 23-25. Please clarify and revise the statement "SOA yield from alpha-pinene, which is a poor SOA precursor near room temperature". I object to this statement as it is currently written. alpha-pinene yields in the literature, coupled with its high emission rate relative to other mono- and sesquiterpenes suggest it is an important contributor to SOA on a global scale even at room temperature (Griffin et al., 1999; Kanakidou et al., 2005)."

AC 10. The authors agree and will change the respective sentence to:

"It was also demonstrated that the SOA yield from alpha-pinene, which produces less SOA near room temperature, has stronger temperature dependence than limonene which produces significant amounts of SOA already at room temperature and above."

RC 11. "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."

AC 11. Figure 7 contains a lot of information. We changed the colour scheme to make it a little clearer.

RC 12. "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."

AC 12. Indeed the influence of relative humidity or absolute water concentration on the yield is not unambiguously demonstrated in the data shown. As already pointed out in our response to a similar comment of Referee 1 we would change the first sentence in section 4.1.5. to:

"From this work a significant impact of humidity on the SOA yields from alpha-pinene ozonolysis, if present at all, can only be taken into consideration for the lowest temperatures investigated."

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A possible mechanistic explanation of the influence of the water vapour concentration on the formation of SOA and especially of pinonaldehyde will be given in the companion paper by Tillmann et al. (2008b) in this journal.

RC 13. "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."

AC 13. We have indeed not seen any direct indication for a delayed oxidation of the second double bond in our measurements with limonene. Ng et al., (2006) did not study the ozonolysis of limonene but interpreted the kinetics of SOA formation in the ozonolysis of terpinolene, which has also a second double bond, assuming slower reactions of first generation ozonolysis products with ozone. Zhang et al., (2006) investigated the ozonolysis of limonene for high and low NOx conditions. For low NOx conditions they did not see a sign of a slow oxidation of a terminal double bond but state that this was oxidised more or less simultaneously with the endo double bond of limonene. This is in agreement with our findings for zero NOx.

AC 14. Due to the length of this paper and since the two companion papers mentioned below are in preparation it seems not reasonable to include more detailed information in this paper on topics that will be addressed there.

Naumann, K. H.: COSIMA-SOA - a model to simulate formation and dynamics of secondary organic aerosol, J. Aerosol Sci, in preparation, 2008.

Tillmann, R., Kiendler-Scharr, A., Mentel, T., Jonsson, Å. M., Hallquist, M., Iinuma, Y., and Saathoff, H.: Water and Temperature Dependence of Pinonaldehyde and OH yields from Ozonolyis of 61537;-pinene, Atmos. Chem. Phys. Discuss., in preparation,

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Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R., Hjorth, J., Kotzias, D., and Larsen, B. R.: Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone, Environ. Sci. Technol., 34, 1001-1010, 2000.

Larsen, B. R., Di Bella, D., Glasius, M., Winterhalter, R., Jensen, N. R., and Hjorth, J.: Gas-phase OH oxidation of monoterpenes: Gaseous and particulate products, J. Atmos. Chem., 38, 231-276, 2001.

Leungsakul, S., Jaoui, M., and Kamens, R. M.: Kinetic mechanism for predicting secondary organic aerosol formation from the reaction of d-limonene with ozone, Environ. Sci. Technol., 39, 9583-9594, 2005.

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, Environ. Sci. Technol., 40, 2283-2297, 2006.

Northcross, A. L., and Jang, M.: Heterogeneous SOA yield from ozonolysis of monoterpenes in the presence of inorganic acid, Atmos. Environ., 41, 1483-1493, 2007.

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Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S. A.: High-resolution mass spectrometric analysis of secondary organic aerosol produced by ozonation of limonene, Phys. Chem. Chem. Phys., 10, 1009-1022, 2008.

Zhang, J. Y., Hartz, K. E. H., 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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