

Interactive comment on “Ozonolysis of α -pinene: parameterization of secondary organic aerosol mass fraction” by R. K. Pathak et al.

R. K. Pathak et al.

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(1) Some data in Table 1 are unclear, missing or incomplete. The whole set of data should be checked carefully. Among others:

- *The alpha-pinene concentration range does not always match the data reported in the literature (e.g. Yu et al. (1999) reported a concentration range of reacted alpha-pinene of 45-57 ppb, lower than the range of 61-110 ppb reported in this table).*

We rechecked the original publications and corrected the small inconsistencies. For example, the initial α -pinene concentration range of Yu et al. (1999) was 59.2-107.1 ppb while the amount of α -pinene reacted was 45-65 ppb. These have all been corrected.

- *The table reports that Hoffmann et al. (1997) have conducted 6 experiments between 48-50 C. However Hoffmann et al. (1997) report 5 experiments conducted between 46*

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and 49 C and one experiment conducted at 16 C.

We made these corrections about the Hoffmann et al. (1997) experiments.

- *Table 1 of Cocker et al., (2001) reports that 11 ozonolysis experiments have been performed in “Low NOx/dark/low RH” (instead of 24 written here) while much more than one experiment have been conducted in “Low NOx/dark/high RH”.*

Cocker et al. (2001) reported the results of 11 experiments with $RH < 2\%$ and 4 more experiments with $RH = 14\%$ which were included in the fit. Also, Fig 3 shows the SOA yields (corrected for water uptake) for 9 other high RH experiments which fall on the low RH curve when the water is removed. These 9 data points were also used in the low RH data set as well. For the high RH data points, there should be 9 experiments and 9 data points (RH range from 31-58%). There were more experiments performed at high RH, but they were at different conditions (different seed type). Only the experiments with no seeds, $(NH_4)_2SO_4$ seeds, or NH_4HSO_4 that were dry were used in the fits for consistency.

- *Only a couple of data points (the final measured AMFs) are reported in the manuscript for the Yu et al. (1999) and Winterhalter et al. (2003) experiments although the data points from the time series measurements reported in their respective paper could be used.*

Unfortunately we did not have the data for the corresponding timeseries and we did not want to try reading the data from the corresponding plots introducing additional uncertainty to these fits.

- *Reference to Griffin et al. (1999) is incomplete (should be Griffin et al.(1999b)) and the data of Ng et al. (2006) for the “Low NOx/dark,/high RH’ conditions are missing.*

We have made these corrections. Actually Gao et al. and Ng et al. discuss mostly the same data points.

- *It seems that Ng et al. (2006) and Lee et al. (2006) discuss over the same ozonolysis*

experiment. However, this needs confirmation. That is correct and is now noted.

- Reference of Pathak et al. (2006) is missing in the bibliography. It is strongly recommended to illustrate this table with figures dedicated to each category of conditions and representing some AMF data points for each experiment in function of the oxidized alpha-pinene. These figures are commonly shown in the literature of this field and it helps the reader to visualize the general trends of the data and to compare the experiments between each other. Predictions of the product-model could be also shown on each of these figures (similarly to Fig. 5).

Pathak et al. (2006) has become Pathak et al. (2007) and it has been updated in the references. These figures suggested by the referee are easy to prepare but they would increase the size of the manuscript without adding much new information. Given that the parameterizations do a good job of reproducing the existing measurements we prefer to use Figures 5-8 instead to help the reader visualize the general trends for the different cases. We have added some discussion of these cases that should also help.

(2) Takekawa et al. (2006) and Kamens and Jaoui (2001) performed photooxidation experiments of alpha-pinene at different temperatures, in a range of 20-60% RH and with HC/NO_x between 1 and 2. Since the oxidation by OH and O₃ are competing in these conditions, the concentrations of alpha-pinene related to the measured AMFs need to be adjusted by the ratio of alpha-pinene actually oxidized by O₃. Model analysis of Kamens and Jaoui (2001) indicate that 41-44% of alpha-pinene has reacted with O₃ in their experiments. Takekawa et al. (2006) do not report any information of this kind. However a ratio of 41% of alpha-pinene oxidized by O₃ is also estimated in the photooxidation experiments of Hoffmann et al. (1997) (Griffin et al., 1999b) with alpha-pinene and NO_x concentrations similar to Takekawa et al. (2006). Would it be possible to obtain a parameterization for “High NO_x/UV/high RH” conditions on the basis of these data?

There is obviously a lot of useful information in these and other similar datasets that

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include both ozonolysis and OH reactions. The idea suggested by the reviewer is solid, but the uncertainty of the corresponding parameterizations would be relatively high given the interactions between the products of the reacting systems. It would preferable to use these datasets that correspond to more realistic conditions for testing of our overall understanding. The parameterizations for high NO_x/UV/high RH experiments would be more reliable for the a-pinene ozonolysis system.

(3) Data analysis regarding the use of a OH-scavenger is missing: As mentioned in page 1950, dark experiments have been conducted with different scavengers: Lee et al. (2006) and Gao et al. (2004) used cyclohexane while the other experiments were conducted in presence of 2-butanol to the exception of Hoffmann et al. (1997) which did not use any scavenger. Keywood et al. (2004) and Jenkin (2004) expect that the type of scavenger affects the aerosol yield up to 50% depending on the concentration of oxidized alpha-pinene. Does the analysis of the data set used in this work confirm this hypothesis? If yes, how to consider this influence in the parameterization? Due to the absence of scavenger in the Hoffmann et al. experiments, 64-94% of alpha-pinene react with O₃ in the chamber. Have the alpha-pinene concentrations been adjusted to take into account the oxidations by OH and NO₃?

One cannot adjust the a-pinene concentrations to account for the oxidation by OH and NO₃ in any easy way. The products from the various reactions all are presumed to form a semi-ideal mixture (and the data support the mixture hypothesis, which has been with us since Odum, at least). This is thus highly non-linear. There is no good way to subtract out the influence of one reaction or the other. The evidence is that the OH a-pinene products are not that different from the ozone-a-pinene products in terms of volatility, and this greatly reduces the errors associated with the secondary pathways.

As for the scavengers, trends with scavengers are not obvious in the broad dataset. Again, nonlinearities combining product chemistry and also the semi-ideal solution make 'correcting' for these effects an extremely challenging proposition. Our approach

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has thus been to recommend the aggregate average as the best current solution for modeling. In the long term, the subsequent chemistry of the compounds left in the gas phase is likely to be a vastly larger uncertainty than the details of chemistry associated with the scavengers.

Specific comments

(4) Page 1942, line 21: Griffin et al., 1999a report that the global average ratio of alpha-pinene oxidized by O₃ is 42.5%. Do you actually mean that the ozonolysis channel contributes for 80% of the SOA produced from the degradation of alpha-pinene (Griffin et al., 1999b)?

Our mistake, yes we mean that ozonolysis contributes 80% of the SOA from a-pinene. This has been corrected in the manuscript.

(5) Page 1947, line 10: Replace “O C to 40 C” by “0 C to 49 C”

We have made the corrections.

(6) Page 1947, line 10: References to Presto et al. (2005a) and Yu et al. (1999) are missing.

The references have been added.

(7) Page 1947, line 19-21: Do you mean that the lower yield of SOA at high NO_x is due to the formation of organic nitrates which have a higher volatility than the compounds (e.g. carboxylic acids) preferably formed in low NO_x conditions? A reference could help to clarify. It is stated that the change in AMFs is “partially” due the formation of organic nitrates. What could be the other reasons ?

High-NO_x chemistry gives different products than low NO_x chemistry. Technically, the product distribution is different (some products are the same, at different yields, some are totally different). Nitrates are unique products in the high-NO_x pathway. It is clear that the aggregate chemistry (possibly including condensed-phase reactions) following

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ozone + α -pinene generates many products, only some of which we have identified. The method followed here does not require knowledge of the products (though that is a laudable goal) but rather infers the volatility distribution based on progressive condensational growth. A brief discussion of these points together with a reference to Zhang et al. (2007) where additional details of these effects (for the limonene ozonolysis) can be found.

(8) Page 1948, line 12: Presto et al. (2005a) state that exposure to UV light reduces the SOA yield by a constant value of 0.03. Please elaborate why the value of 0.06 is adopted.

The typo has been corrected. The correct value is 0.03.

(9) Page 1951, line 11: The choice of the averaged molecular weight equal to 150 g/mol seems low. Identified compounds in the particulate phase such as pinonaldehyde (MW=168 g/mol), pinic acid (MW=186 g/mol), pinonic acid (MW=184 g/mol), hydroxyl pinonic acid (MW=200 g/mol) or organic nitrate compounds (MW >170 g/mol) have a molecular weight higher than 150 g/mol.

This is a valid point. To avoid these issues with the choice of an average molecular weight the basis set formulates Raoult's law for organic mixtures in terms of molality (as opposed to molarity – See Donahue et al EST 2006 supplemental material). Any assumptions about average molecular weight should be viewed as placeholders to allow things to fit into current implementations.

(10) Page 1951, Eq. 2: The term $Y_{j,\text{fitted}}$ would be more appropriate than $Y_{j,\text{predicted}}$ since the objective is to obtain a fit of experimental data. It is not very clear from Eq. 2 which data are used. Referring to line 1 (page 1951), it seems that only one Y value is taken into account for each j experiment. However, the comparison between the “predicted” and the measured AMFs in Fig. 4 suggest that all the data points have been considered.

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We have changed the “predicted” to “fitted” and we have clarified that for some experiments multiple values are used in the fitting.

(11) The experiments are not given the same weight in the minimization since their related number of data points vary significantly. For example, the parameters for the “Low NOx/dark/humid” conditions correspond essentially to the regression of the experimental data of Gao et al. (2004) (177 data) rather than the other studies (25 data). It may be difficult to provide parameters deduced from a minimization in which each experiment has the same weight, since many of them provide too few data points. However it is recommended to calculate the sum of the averaged relative errors between the model and the data of each experiment weighted by the total number of experiments for each specific condition. This weighted relative error would provide information regarding the reproducibility of the experiments as well as the capability of the model to simulate a typical experiment for a given category of conditions. The classification of the conditions underlying the regression modelling could then be evaluated.

This is an excellent point, but as the reviewer also realizes there is no easy solution. Providing equal weight to all experiments is “unfair” to the experiments that provide several data points and thus more information. We have decided to treat each data point equally even if this is probably “unfair” for the experiments that provide only one value. The optimum approach is probably somewhere between these two extremes. Our solution to this, has been a method to estimate the uncertainty of the fits (Stanier et al., 2007, in preparation) and therefore an approach to determine if our approach biases the outcome of the analysis by giving too much weight on the experiments providing several data points.

(12) page 1951, line 25: Torr or Pascal units are more commonly used for the vapour pressure.

It is true that saturation levels are usually expressed as partial pressures. However, for the basis-set the use of mass concentrations is clearly preferable. The basis-set

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is used to for the calculation of the organic aerosol concentration (which is expressed traditionally as mass concentration). The use of mass concentration units allows then the direct link of the ambient organic aerosol concentration with the fraction of each basis-set component in the particulate phase. We have added in parenthesis the corresponding mole fractions and partial pressures to help the readers used to the vapor pressure units.

(13) Fig. 3. The data from the experiments of Gao et al. (2004) is missing in the figure. This group reported absolute SOA yields between 0.32-0.35 for a range of alpha-pinene of 25-48 ppb at 20 C. Ng et al.(2006) do not report ozonolysis experiment of alpha-pinene conducted at RH = 55%. Could you be more precise about the source of these data?

The confusion here is that the same data were the basis of both papers by the Caltech group, but some were presented and discussed in detail in the first and some in the second paper. The authors were kind enough to provide us with the complete dataset and that is why we reference both papers. Ng et al. (2006) plot the low NO_x/dark/humid experimental data in Figure 5 of their paper. We have added a sentence explaining the situation and the need to reference both papers.

(14) The use of the same value for the enthalpy of vaporization for conditions others than “low NO_x,/dark/humid” would be justified by similar graphic representations.

The enthalpy of vaporization was used as a parameter of the fitting procedure. Different values were used and the one providing the best fit was used. Only for the high RH case there was a need to use a larger ΔH value to fit the experimental results.

(15) Fig. 4. The model and the measurements show a very good match except in the “Low NO_x/dark/low RH” conditions where the model underestimates the measured AMFs at high values up to a factor 2, in contrast to the averaged error of 15-20%. What is the reason of this important disagreement?

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This disagreement is due to a single experiment reported by Hoffmann et al. (1997) conducted at 16 C). The authors reported an SOA AMF of 0.67 at 16 C for 90 ppb of α -pinene, which is unusually high compared to the values reported by other researchers (Pathak et al. 2007). It has been impossible to find a parameterization fitting this point together with the rest of the dataset. It could be an outlier or sign of something interesting that happens in these relatively high concentration conditions. This point is now discussed briefly in the revised manuscript.

(16) *Fig. 5. Please mention the temperature adopted in the model.*

We are using 298 K and this is not mentioned in the caption.

Technical corrections

(17) *Reference to Fig. 3 comes before Fig. 2 in the text.*

The missing reference to Figure 2 has been added.

(18) *Page 1954, line 27: Replace “hydrocarbon” by “hydrocarbons”*

Done.

(19) *Page 1956, line 9: “(16)” not necessary.*

It has been deleted.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 1941, 2007.

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