Atmos. Chem. Phys. Discuss., 7, S400–S405, 2007
www.atmos-chem-phys-discuss.net/7/S400/2007/

Atmospheric
Chemistry
and Physics
Discussions

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

Anonymous Referee #3

Received and published: 5 March 2007

General comments

This manuscript presents 4-product and 7-product regression models relating the observed dependence of the aerosol mass fraction (AMF) with the alpha-pinene concentration in laboratory experiments of ozonolysis. This new set of parameterizations improves previous model representations since it is based on a wider set of experimental data collected in various conditions and its provides temperature dependences of the AMF yields. Estimations of the AMFs produced from the O3-oxidation of alpha-pinene are made possible for 5 different categories of atmospheric regimes defined by the NOx concentration (“high” or “low”), the presence of light (“UV” or “dark”) and the relative humidity (“high” or “low”). Unfortunately, no parameterization is provided for the “High NOx/UV/high RH” conditions although these are common in the atmo-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

sphere. Experimental studies have shown that the oxidation of alpha-pinene produces non negligible amounts of secondary organic aerosol (SOA) in these conditions as well.

The approach consisting in the development of temperature dependent models for different categories of chemical conditions is valuable and it will clearly improve the estimations of SOA concentrations in chemical transport models. However, the data analysis on which the regression study is based seems not very rigorous. Some points described below should be tackled before publication in ACP: 1/ The presentation of the experimental data on which the parameterization is based would need substantial revisions. 2/ A discussion over the impact of the OH-scavenger is required. 3/ A discussion over the parameterization for the “High NOx/UV/high RH” conditions should be also included in this work.

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). -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 and 49 °C and one experiment conducted at 16 °C. -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”. -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. -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. - It seems that Ng et al.(2006) and Lee et al.(2006) discuss over the same ozonolysis experiment. However, this needs confirmation. - 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).

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/NOx 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 NOx concentrations similar to Takekawa et al.(2006). Would it be possible to obtain a parameterization for “High NOx/UV/high RH” conditions on the basis of these data ?

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 ?

Specific comments

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) ?

Page 1947, line 10: Replace “O°C to 40 °C” by “O°C to 49 °C”

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

Page 1947, line 19-21: Do you mean that the lower yield of SOA at high NOx is due to the formation of organic nitrates which have a higher volatility than the compounds (e.g. carboxylic acids) preferably formed in low NOx 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 ?

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.

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 pinonalhehyde (MW=168 g/mol), pinic acid (MW=186 g/mol), pinonic acid (MW=184 g/mol), hydroxy pinonic acid (MW=200 g/mol) or organic nitrate compounds (MW $>$170 g/mol) have a molecular weight higher than 150 g/mol.

Page 1951, Eq. 2: The term Yj,fitted would be more appropriate than Yj,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.

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.

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

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 use of the same value for the enthalpy of vaporization for conditions others than "low NOx,/dark/humid" would be justified by similar graphic representations.

Fig.4. The model and the measurements show a very good match except in the "Low NOx/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 ?

Fig.5. Please mention the temperature adopted in the model.

Technical corrections

Reference to Fig. 3 comes before Fig. 2 in the text.

Page 1954, line27: Replace “hydrocarbon” by “hydrocarbons”

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

References

Kamens, R., and M. Jaoui Modeling aerosol formation from alpha-pinene + nox in the presence of natural sunlight using gas-phase kinetics and gas-particle partitioning theory, environ. sci. technol., 35, 1394-1405, 2001.

Keywood, M. D., J.H. Kroll, V. Varutbangkul, R. Bahreini, R. C. Flagan and J. H. Seinfeld, Secondary Organic Aerosol Formation from Cyclohexene Ozonolysis: Effect of OH Scavenger and the Role of Radical Chemistry, Environ. Sci. Technol, 38, 3343-3350, 2004.

Jenkin, M. E., Modelling the formation and composition of secondary organic aerosol from alpha- and beta-pinene ozonolysis using MCM v3, Atmos. Chem. Phys., 4, 1741-1757, 2004.

Takekawa, H., H. Minoura, and S. Yamazaki, Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, Atmos. Environ., 37,3413-3424, 2003.

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