**Atmospheric
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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) Section 2, p. 1946, Section 2.3, p.1947, Section 2.4, p. 1948 I have difficulties to accept the notation "ozonolysis at high NOx" for the reaction of a-pinene with NO_3. In many of the high NOx cases NO_3 will clearly dominate the a-pinene consumption, and the reaction products contribute to the SOA mass (Presto et al., 2005b). The potential role of NO_3 (and its potential effect on the ai compared to ozonolysis products) must be discussed.

The potential role of NO_3 is discussed in detail in the Presto et al. paper. The evidence is that NO_3 is at most a secondary contributor to the observed chemistry. It certainly can not explain the very large decreases in SOA observed at low VOC:NOx. The most significant evidence cited in Presto et al to this effect is that the a-pinene loss rate is always consistent with the known a-pinene+ozone rate constant, with rates between

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1x and 1.25x the expected value. This indicates that NO_3 is responsible for at most 20 percent of the a-pinene removal.

The rate constant for a-pinene + ozone is 3 times the rate constant for NO_2 + ozone (to make NO_3), and that the experiments typically had NO:NOx > 0.5. Thus, for VOC:NOx = 5:1 (ppmC/ppm) the simplest kinetic model suggests that ozone removal should be 3 times the NO_3 removal. This assumes no NO_3 photolysis and no N_2O_5 sink. The (indirect) evidence is that some combination of these later two processes is also important, because 'extra' a-pinene removal is never even so large as the simple mass-balance model would suggest. The bottom line is that NO_3 does represent a source of uncertainty, but it is a secondary channel in these experiments and it does produce condensible products. There are larger uncertainties in the overall problem.

(2) Section 3.1, p. 1951 To me the start condition and the use of the ΔHv vector is not quite clear. In principle with changing temperature the set of α_i should be shifted left/right over the basis set. Why is $\Delta Hv=70$ kj/mol so large for low NOx, high RH ?

This is a good point. In the current basis set formulation the stoichiometric coefficients a_i are assumed to be temperature independent over the temperature range of applicability of the parameterization. The temperature dependence of the SOA formation is therefore mainly described by the "effective" ΔHv. One ΔHv value is used for all the basis-set compounds. All of these are of course simplifications of the actual situation. The error introduced by assuming that the ai are temperature independent can be estimated by comparing the results of experiments performed at one temperature with the results of experiments performed at say room temperature and then change of the temperature to the temperature of interest (Pathak et al., 2006). The validity of the use of one ΔHv value can be estimated from the comparison of the fitted results at different temperatures with the measurements (see for example Figure 4). The result of all of this is that the ΔHv may also account for the change of the a_i with temperature, and that is why it should be viewed as an "effective" ΔHv that is useful for the parameterization of the results. This potential hidden dependence makes the detailed discussion

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of its trends dangerous.

The above important points are now discussed in the revised paper.

(3) Section 3.2 and Table 3 Can we learn something from the systematics of the a_i e.g. of 7-basis set for the processes in the regimes? Why is the 7-basis set of low NOx, dry so similar to the high NOx, dry and high NOx, wet cases, although the AMF is much larger. Why is it so different from the low NOx, wet case, although the yields are similar (Fig. 6). What is the role of the $\triangle Hv = 70$ in the latter case?

This is one more good point. Comparison of the coefficients for the low NOx dry and high NOx parameterizations suggest that three of them are very similar to each other (compounds 5 to 7) while the other four are quite different (compounds 1 to 4). The much higher yields of the low volatility components of the basis set for the low NOx case result in a much higher AMF at the corresponding low organic aerosol levels (less than 10 μg m^{-3}) where the high volatility components play a negligible role (they are mostly in the gas phase). We believe that the difference for components 1-4 is real. On the other hand, the yields of the components 5-7 in the high NOx case are not well-constrained because there are almost no experiments available where these components are a major component of the organic aerosols. So the similarity of these may be real or may be just a numerical coincidence.

The opposite happens with the low NOx dry and wet cases. In this case the low volatility products have similar yields but the high volatility products have different ones. This results in similar behavior in the atmospherically relevant low concentration regime (shown in Figure 6) but different AMFs at the higher concentration range (not shown). Also these are applicable to the reference temperature. The different effective $\triangle H$ values result in changes of the above relations as the temperature changes.

We have added discussion of these issues (something requested by the 1st reviewer too) after the presentation of the different parameterizations.

(4) Section 3.2 and Fig 4 a) b) d) There are some systematic deviations of groups of data (probably) from the 1:1 line, always in direction of overestimation by the model. Do these reveal aspects not catched by the chosen initial conditions? Do they contain helpful information? A representation and discussion of the quality of the reproduction of temperature dependence is missing.

The groups of data correspond in almost all cases to sets of measurements by the same research group. There are both underestimations and overestimations by the model (e.g., in Figure 4a the model is underestimating a little several low AMF experiments and overestimating compared to one of the high concentration experiments). We have not placed error bars in the experimental results (a lot of them are not ours and the authors did not publish error estimates) but most of the discrepancies are within the expected experimental error (reflecting just the reproducibility) of most smog chamber experiments. Given these small discrepancies we do not think that there is much useful information in these differences.

We have added a few sentences discussing these differences and the good reproduction of the temperature dependence by the parameterizations.

(5) Figure 1,2,4 are too small and should be color coated. The fonts in all Tables are too small, in Table 3 it is much too small.

We have noted these points and we will correct them in the final version of the paper.

(6) References Koo et al. 2003 is missing and Pathak et al. 2007: title is wrong.

The Koo et al. reference has been added and the title of the Pathak et al. reference has been corrected.

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