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Interactive comment on “Determination of alpha;-pinene-derived organic nitrate yields: particle phase partitioning and hydrolysis” *by* J. D. Rindelaub et al.

Anonymous Referee #2

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This is an interesting manuscript that reports organic nitrates in the gas phase and in particles from the ïĄą-pinene reaction with OH in the presence of NOx and their loss which is attributed to hydrolysis in particles. These seem like very difficult experiments, but have certainly generated interesting results.

This reviewer found some of the distinctions made by the authors difficult to follow from the data they show. For example, Figures 3 and 4 show organic nitrate yields as a function of relative humidity. The data for the acidic and unseeded case at low RH (about < 15% RH) are very scattered, covering factors of $\sim$ 3-5. Are there some experimental reasons for this large amount of scatter?

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It is not clear from the figure caption whether each point represents one experiment or an average of several (i.e., does "multiple experiments" mean each point is one experiment or each is an average of a number of experiments?). Assuming each point is one experiment, would it not make more sense, given the scatter, to average these lower RH experiments and show error bars in both the X- and Y- axes, with the data from individual runs in a table to show the ranges?

With this much scatter, it is not at all clear how they could carry out a linear regression on the low humidity data (what range did they use?) to get a yield from the Y-intercept, particularly to give an error of only 6% on the yield of 23% they derive. The scatter at low RH for the unseeded aerosol (Fig. 4) is about the same as for the acidic aerosol (Fig. 3) but clearly the intercept in Fig. 4 at low RH would be very hard to determine.

Figure 6 shows organic nitrate yields separately for gas and aerosol. It would be helpful to show the paired data, i.e. in one experiment, what are the values for each? I think this is essentially what is shown in Fig 7, so they might just refer to that in discussion of Fig. 6. If this interpretation is correct, it looks like the ratio of gas to particle nitrate varies by three orders of magnitude for each set of experiments at RH below 40%. A question then is what can be derived from the data with this much scatter.

Much of the last part of the paper is devoted to a discussion of mechanisms and possible products. However, no product data is given (could they not obtain information on specific products from their GC-NICI-MS measurements?), except to say the one product they looked for that might be expected from the nitrate product reaction (pinanediol) was not observed. Given the lack of product data, the extensive discussion of potential mechanims and products and five reaction schemes seems inappropriate.

This reviewer found the discussion of partitioning confusing. The calculated time for uptake into the particles is 194 s, which is relatively short on the time scale of their experiments so that equilibrium between the gas and particle phase should be achieved. However, they state that the plot of Fi/Ai against aerosol mass that should be linear in this case is "highly scattered and does not show such a relationship... cannot be explained by a simple gas-particle equilibrium model". If the plot is that scattered (it is not shown), can they be confident that it really rules out the equilibrium model? And if it is not, what are the alternatives and what would the data be expected to show in that case? On page 13, line 288, the sentence beginning "Then, to maintain equilibrium, uptake of gas phase organic nitrates to the particle phase will occur...." implies that there is equilibrium partitioning occurring, while it was argued a few lines above that it does not. Similarly, in "Conclusion", it says "The concentration of organic nitrates present after equilibration with particles ..." and also that at high relative humidity, "liquid-like particles where equilibrium partitioning readily occurs.." This reviewer is confused about whether the authors believe equilibrium partitioning occurs, and if so, what data show this, also why the statement is made that the data are not consistent with this. A related statement in the Conclusion is that "hydrolysis alone does not account for all the variability in the Kp values"; it is not clear to this reviewer what this statement is based on.

Experimentally, there are several questions: 1. Page 5, line 107: The chamber was flushed with air to clean it. Is this enough? Matsunaga and Ziemann (Aer. Sci. Technol.) showed that Teflon takes up organics, particularly polar species that would be formed in these reactions, and releases them back into the gas phase. Could this be responsible for the non-linear plot of aerosol mass vs time in Fig. 2 where there seems to be more mass than expected initially? 2. The infrared spectrum in Fig. 1 shows a number of strong peaks that do not appear to be the CCl4 solvent, but surprisingly, they appear in the filter blank as well. Can the authors comment on these? Also, some are saturating at an absorbance of 2.5 and even the nitrate peak at 1640 cm-1 is quite strong, with an absorbance of about 1.3. The latter corresponds to only 5% of the analytical light beam getting through the sample and under these conditions, signals are often non-linear with concentration. This has probably been considered by the authors but a comment on this would help the reader. Would use of a cell of length less than 1 cm be appropriate? 3. Page 7, line 151: Because the particles grew rapidly beyond

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the SMPS limit, they were "unable to calculate aerosol yields or partition coefficients for the unseeded experiments". Could the sampling be done at shorter times before they have grown this large, or could the initial precursor concentrations be lowered? 4. Does the denuder strip only gas phase organic nitrates or can it also evaporate these compounds from the particles as they pass through? 5. What were the number and mass concentrations of the initial seeds? 6. Page 10, line 235: "The gas phase yields were not dependent on seed aerosol composition". It appeared to this reviewer that only the acidic seed data are shown (Fig. 6), perhaps it should be shown for all cases?

Technical/minor comments:

1. Page 4, line 81: The Chen et al. (1998) reference is not in the reference list. 2. Page 4, line 92: Should "glass tee" (as in golf tee) be "glass T"? 3. Page 6, line 124: Need space between the number and unit in "1 cm". 4. Figure 2: Rather than saying "a representative experiment", more details should be given in caption. For example, text says "a seed aerosol" experiment but in neither the text nor caption which seed was used is given.

Overall, this paper has much to like about it and many of the comments can likely be addressed by clarifications in the presentation.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 3301, 2014.