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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* “Hydrolysis and gas-particle partitioning of organic nitrates formed from the oxidation of $\alpha$-pinene in environmental chamber experiments” *by* J. K. Bean and L. Hildebrandt Ruiz

**Anonymous Referee #1**

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Review of Bean & Hildebrand, “Hydrolysis and gas-particle partitioning of organic nitrates formed from the oxidation of a-pinene in environmental chamber experiments”, ACPD 2015

This paper presents a novel series of chamber experiments, in which organonitrate aerosol is generated via photo-oxidation of $\alpha$-pinene, at varying RH. The paper presents gas/aerosol partitioning coefficients and hydrolysis rates of organonitrates derived from a combination of observations and modeling. While I have some questions

about the determination of these parameters from the available observations, this is a topic of great interest and importance to understanding tropospheric ozone production and addresses questions particularly relevant to the growing literature working to interpret discrepancies between regional / global models and observations of organonitrate aerosol. Some expansion of the discussion including uncertainty analysis will help put this work in context for the community. The paper is cleanly written. In this reviewer’s opinion, fleshing out some methodological detail would be beneficial.

General comments:

1) The statement about observed hydrolysis rate in the abstract does not match your discussion and last figure, which suggests a dependence of hydrolysis on RH. I think this rate should be reported cautiously and I would avoid stating a cutoff for hydrolysis given the lack of reproducibility in your measurements near 22%.

2) P. 20635, re: wall loss correction: How would this correction be affected if wall loss rates depend on RH (likely) or are different for different chemical species?

3) P. 20636, obtaining mixing ratio of aerosol nitrate: Please flesh out explanation of this. Did you take mass loading of each NO and NO2 separately and use those fragments’ MW’s to convert to mixing ratios, which you then summed? Doesn’t the AMS calibration assume that both NO and NO2 come from NO3 functional groups and therefore the MW to use to do the conversion would be that of the NO2 fragment, since it is assumed the O-N bond breaks and one of the O’s would be detected amont the organic fragments? Please clarify what you did and be sure that the assumptions are correction – this could give big errors in the mixing ratios and consequently change the partitioning coefficients substantially!

4) Ibid. I have serious reservations about the accuracy of the determination of gas-phase organonitrates from mass balance. This assumes there are no other N-containing species, such as HONO or NO3 and N2O5, which could certainly form in your experiments. Photolysis of these may be fast, but so might the production rate.

You could include these in your model to show their expected concentrations and then determine whether they could be a source of error to your N balance. At least in the supplemental material, please show one of your time series of the partitioning coefficient.

5) P. 20637, discussion of hydrolysis rate: From Darer et al, it appears that tertiary nitrates should have rapid hydrolysis rate constants and primary should be quite slow. Boyd et al ACPD 2015 have used this to estimate in the case of NO3 + $\beta$-pinene, what fraction of the NO3 radical additions occur at which end of the double bond. This might be worth discussing here. Do you assume that all of your nitrate is tertiary and compare to the literature based on that? Is there any literature basis for a faster rate than the one you assume in your assessment of whether the gas/aerosol partitioning could be affected by hydrolysis? My sense was that these rates are not well known. You conclude hydrolysis can't affect partitioning – is this because the assumed hydrolysis rate was slow relative to the timescale of these experiments? Given the uncertainties in hydrolysis rates, you could flip this analysis around and ask instead, how fast does the hydrolysis have to be to change the partitioning coefficient by X%? Perhaps in addition to what you have here. This would give future researchers a quick comparison point – if they determine a faster rate, this provides a quick assessment of whether that rate is partitioning-relevant.

6) P. 20639, interpreting the <0 values: You mention the possibility of HNO3 contributing to aerosol nitrate. A calculation using Henry's law coefficient for HNO3 will allow you to determine whether this could be happening.

7) P. 20640, interpreting temperature ramps: Were these only done during the early states of oxidation, while the partitioning species would be the less oxidized and thus more semi-volatile? Or did you try this at different delay times to investigate the effect of increasing oxidation on (presumably) decreasing volatility?

8) P. 20642 bottom, discussion of observation of decrease in both organics and nitrate:

why should PM organics also decrease? Hydrolysis producing HNO3 would certainly be expected to volatilize the nitrate, but mightn't the organic left behind be expected to stay in the condensed phase? Can you learn anything from the relative rates of loss of organic vs NO3?

9) Ibid, + around p. 20643 line 1-3: please explain how you obtained these hydrolysis rates- just the decay rate of NO3 aerosol? Or normalized to SO4?

10) Table 1: Looking at the hydrolysis rates here for RH = 22, 15, and the two 70's, I am not convinced of the reproducibility at a given RH. This either just means the rates are not known that well, or that RH is not the determining factor. Either way, I think this suggests a retreat from Fig. 5, which implies that there is a correlation between RH and NO3 loss rate.

11) Figure 2 is puzzling to me. Why don't the intermittent green traces match their previous trend? You interpret this as meaning that the more oxidized species are monotonically increasing, but that is not apparent here; they appear to have decreased around 200 minutes. This requires more explanation/interpretation.

12) Figure 3: the re-increase of the particle phase signals after cooling that you mention in the text isn't super clear to me here – clearer is the gas phase loss. Maybe this suggests that the re-condensing species are mostly partitioning to the walls? Could discuss in terms of relative SA of particles vs. walls.

13) Figure 4 comparison: Is the Rollins et al VBS fit also based on mole fraction, not mass fraction? Could this matter here for the discrepancy?

14) Suggest to omit Figure 5. I'm not convinced RH is the driving factor here.

15) Supplemental Fig. S2: O3 goes up quite a bit over your experiments – could this compete with OH for your $\alpha$-pinene? Or react with NO2 and affect N balance (this is where I started wondering about whether N2O5 could be another part of the N balance story). Is NO2+O3 in your SAPRC model?

Specific technical suggestions:

1) P. 20631 lines 6 and 10: commas missing after ()'s

2) Ibid line 16: please mention the RH and oxidation scheme of Liu et al. here, to help the reader put this in context.

3) P. 30633 line 7: Sounds like the experiments were run in batch mode. Was there a dilution flow or was the chamber allowed to collapse? How long did injections take? Was anything continuously injected?

4) P. 20634, line 7: mention frequency of ion scheme switching and rationale

5) Ibid, around line 16: How much / did RH change over the course of experiments? This would be useful to state here in terms of interpreting CIMS data (isn't there a strong H2O dependence in I- sensitivities?), especially in interpreting the timeseries in Fig. 2 – perhaps add a panel with RH time series to that figure?

6) Ibid, line 18: NOx measurement is chemilum, but O3 is probably absorption?

7) P. 20638: eqn 1: Don't Donahue et al use the greek symbol xi for fraction, rather than Y?

8) P. 20639 line 18: Is the timescale of initial product formation consistent with the expected rate of RO2 formation and RO2+NO?

9) P. 20640 line 11: Sulfate → H2SO4, correct?

10) P. 20641 line 2: refer to figure for observed particle-phase trends

11) P. 20642 line 11: careful about overgeneralizing this result – add clause that this observation is specific to ON from photooxidation of $\alpha$-pinene.

12) Table 1: define Part Coeff briefly in the caption, stating that its molar not mass, to avoid possible misinterpretation by someone scanning the paper.

13) Figure 1: please indicate in the caption how each trace is determined: measured

directly, determined subtractively, modeled.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 20629, 2015.