

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

Anonymous Referee #2

Received and published: 6 October 2015

This study aims to investigate the hydrolysis and gas-particle partitioning of organic nitrates formed from the photooxidation of α -pinene. Experiments were performed under varying RH. By adjusting the temperature during the experiments and observing the corresponding changes in the gas and particle-phase composition, the authors proposed that the ON gas-particle partitioning is reversible. By calculating the decay rate of particle-ON, the authors determined that the particle-phase ON hydrolyzes with a rate of 2 day⁻¹ at a RH of 22% or higher.

C7621

With the important roles of organic nitrates in NO_x cycling and ozone formation, etc. this work would be of interest to the community. The experiments themselves are interesting, however, I found the data analysis and interpretation over-simplifying, and in many cases, over-reaching (please see detailed comments below).

The calculation of gas-particle partitioning is subjected to many uncertainties. The authors simply attributed all the observations as a result of temperature change to gas-particle partitioning, without recognizing/discussing the various processes that could also potentially contribute to changes in gas and/or particle-phase composition. All these need to be thoroughly discussed and addressed in the manuscript as they can potentially change the conclusions of the manuscript.

The same comment applies to the determination of the hydrolysis rates of organic nitrates. The authors attributed the decay in particle-ON to hydrolysis without addressing the effects of other processes. There appears to be large uncertainties in the calculated decay rates, where experiments with similar reaction conditions have very different decay rates. With results from recent studies related to organic nitrate hydrolysis (e.g., Rindelaub et al. (2015) and Boyd et al. (2015)), it appears that whether the organic nitrates are primary/secondary/tertiary plays an important role in their overall hydrolysis rates. While Rindelaub et al. (2015) did not report a hydrolysis rate directly, it seems that the particle-ON formed in the current study hydrolyzes at a much slower rate than those in Rindelaub et al. (2015). More discussions are needed.

Overall, while the experiments are interesting, the manuscript needs to be greatly revised to reflect the proper and appropriate conclusions one can draw from the data (i.e., not going beyond what they can conclude from the data), as well as carefully addressing the associated uncertainties.

Specific Comments

1. Page 20636, line 21. The authors noted that the NO and NO₂ fragments were converted to ppb using the molecular weight of these fragments. I do not think this is

C7622

correct. The NO and NO₂ mass concentrations are nitrate (-ONO₂) equivalent mass, so to convert them into molar basis, the molecular weight of -ONO₂ should be used. If the authors indeed calculated the mixing ratios incorrectly, it would change the partitioning coefficients and affect the conclusions of the manuscript.

2. Page 20637, section 2.2. The calculation of partitioning coefficient is subjected to many uncertainties, which should be discussed in detail and the authors should evaluate how such uncertainties might affect the conclusions of the manuscript.

a. It is assumed that only five major forms of oxidized nitrogen are present. As this assumption forms the basis of the subsequent analysis, the authors need to justify this assumption. Other nitrogen-containing species can be formed in their experiments, e.g., NO₃, N₂O₅, HO₂NO₂ (especially H₂O₂ is used as OH precursor, which would lead to formation of a large amount of HO₂), HONO, etc. These species could be photolyzed or react with OH, but the authors need to provide justifications that all other nitrogen-containing species are negligible. If not, how would this affect the calculation of partitioning coefficient?

b. It is noted that the H₂O₂ concentration used in the model was adjusted until the modeled NO, NO₂, and O₃ matched experimental data. Firstly, why is the H₂O₂ concentration not an input? Based on the experimental description, the concentration of H₂O₂ should be known (e.g., can be calculated from the injected H₂O₂ volume and chamber volume). Secondly, as seen in Table 1, the modeled H₂O₂ has a large variation. Is this expected? i.e., did the authors inject different amounts of H₂O₂ into the chamber in different experiments? If so, what are the H₂O₂ concentrations injected (this info needs to be included in the table)?

c. If the H₂O₂ concentration indeed varies that much, it would seem very likely that the fraction of α -pinene reacting with OH vs. O₃ also varies from experiment to experiment. Would different types of organic nitrates be formed in different experiments, depending on the reaction pathways? If so, how would this contribute to the calculation of the

C7623

partitioning coefficient of organic nitrates as a whole?

d. Related to the previous comment – from Figure S2 it appears that the ozone concentration is quite high. Is the α -pinene concentration measured? If so, it should be included in Figure S2.

e. This comment is not just relevant for the determination of the partitioning coefficient, but also relevant for the evaluation of organic nitrate hydrolysis. ACSM is a unit mass resolution instrument and cannot differentiate ions at the same mass. E.g., m/z 30 can be CH₂O⁺ and NO⁺. Here, I guess the authors assume that all m/z 30 is from NO⁺. How did the authors justify this assumption? It has been shown that for organic nitrates formed from β -pinene+NO₃ (Boyd et al., 2015), the organic CH₂O⁺ fragment accounts for a fairly fraction of the total signal at m/z 30. If this applies for the current study, the particle-phase organic nitrate would be over-estimated, which would affect the calculated partition coefficient. It is possible that the organic interference at m/z 30 would depend on the particular system. However, the authors need to discuss what does this mean for their data analysis and conclusion.

3. Page 20639. Figure 2. Are these the only organic nitrate species measured in the experiments? Please clearly state this in the manuscript.

4. Page 20640, discussion on gas-particle partitioning. The authors changed the chamber temperature to evaluate the reversibility of organic nitrate partitioning. The authors attributed all observations as a result of gas-particle partitioning, which I think is over-simplifying and not very convincing. I focus my comments on Figure 3 here.

a. First, what is the time series of α -pinene concentration? When the temperature perturbation occurred (~240 min), has all the α -pinene reacted? As seen from the figure, during the period between UV off and temperature increase, there is still an increase in org/SO₄, which would seem to suggest α -pinene is still being reacted and SOA is still being formed? If α -pinene has not all been reacted away, can some of the trends we are seeing here a result of on-going reactions?

C7624

b. The authors attributed the increase in gas-phase species as a result of evaporation of these species from the particle phase at higher temperatures. In the figure, during the warming period, all the particle signals decreased, however, some of the gas-phase signals reached a maximum first and then decreased, why? It seems that there is more than gas-partitioning going on here.

c. At about ~320 min, the temperature decreased. The authors attributed the decrease in gas-phase signals to repartitioning of these species to the particle phase. However, the increase in the particle-phase concentration is not as substantial (much lower than pre-temperature ramp loading). Why?

d. What is the role of gas-phase wall loss in these observations? One can also argue that the change in gas-phase species (in Figure 3c) can be affected by gas-phase wall loss.

5. Page 20642 onward, I do not think that the authors can make any definite conclusions regarding organic nitrate hydrolysis based on their data.

a. Line 22. Why did the concentration in Expt 1 continue to increase? Please explain.

b. In determining the rate of decrease in particle-ON, I assume the chamber lights are off? (otherwise further photochemical reactions can affect gas and particle-phase composition).

c. If the lights are off, are there nitrate radicals in the chamber, are there any further reactions induced by the nitrate radicals?

d. The authors need to show the decay (raw data) of the nitrates in the SI, and show clearly how the decay rate is determined.

e. What does the "decay rate" mean for experiments with RH=0% (Expts 8 and 9)? Do the authors think that's also from hydrolysis? If so, where does particle water come from? The ammonium sulfate seeds should be solid for a chamber RH of 0%.

C7625

f. Overall, the authors attributed the decay in nitrates to hydrolysis. To do so, the authors must first justify that no other processes or reactions can contribute to the decay of the nitrates (e.g., comments b and c, etc)

g. One way to evaluate hydrolysis rates would be to normalize the decay in nitrates in the humid experiments to those in dry experiments, similar to the analysis in Boyd et al. (2015). Have the authors look into this?

h. What are the uncertainties of the data points shown in Figure 5? Is there supposed to be an increasing trend, or the authors think that the loss rate should be constant? Why? Either case, more justifications and discussions are needed.

i. The authors noted that Expt 10 is an exception, "possibly due to effects of being near the deliquescence relative humidity for that particulate aerosol". Firstly, do the authors mean the DRH for ammonium sulfate, or the organic + sulfate aerosol? The DRH for ammonium sulfate is ~80%, so at the experiment RH of 70%, the ammonium sulfate should be solid? Secondly, the experimental conditions in Expt 10 and Expt 11 are very similar, yet the loss rate is drastically different? Why? This goes back to the previous comment, what are the uncertainties of the decay rates?

j. Page 20643, lines 9-15. The authors need to discuss how the hydrolysis rate determined in this study compared to those reported in recent literature. For instance, Rindelaub et al. (2015) studied the formation of organic nitrates from photooxidation of α -pinene (same as this study). While Rindelaub et al. (2015) did not report a hydrolysis rates for organic nitrates, their results suggested that organic nitrates formed from α -pinene+OH+NO_x appear to hydrolyze fairly quickly, which is different from the current study? Please discuss. Furthermore, Boyd et al. (2015) reported that majority of the organic nitrates formed from β -pinene+NO₃ are primary/secondary nitrates and are stable, while ~10% of the organic nitrates are tertiary and hydrolyze on the order of few hours. The hydrolysis rates determined in the current study is fairly slow, are the authors implying most of the organic nitrates formed are primary/secondary? (this

C7626

would seem to contradict the results by Rindelaub et al. (2015)?

Technical Comments

1. Page 20631, lines 9-18. Here, the authors should also mention the studies by Rindelaub et al. (2015) and Boyd et al. (2015), as both studies discussed the hydrolysis of organic nitrates in aerosols.

2. Page 20640, line 18. It should be "Figure 3c"?

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

C7627