

Interactive comment on “Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields” by A. W. Rollins et al.

N. L. Ng

ng@aerodyne.com

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This is an interesting study and it provides new insights into SOA formation from isoprene and nitrate radicals. I have two main comments regarding the citation of previous work, and SOA composition data measured by the AMS. The authors compared some of their findings to a previous study by Ng et al. (2008). However, the way certain sentences are phrased seems to imply inconsistency between the current study and Ng et al. (2008), but without detailed explanations (and in many cases I do not think that the results from the two studies are inconsistent). The authors need to be more specific when they compared the two studies to avoid misinterpretation of previous work. Regarding AMS data, one of the main results from this study is that the “nitrate” content measured by the AMS is much lower than one would expect from the structures of the

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SOA products. However, the analysis of the AMS data is not explained in detail and more description/discussion is needed.

Some comments: 1. Did they only perform one experiment? It's not very clear from the manuscript, but it seems to me that they only did one experiment. How can the authors be sure their results are reproducible?

2. Page 8862, line 25. The chamber RH is 57%. In Ng et al. (2008) the experiments were performed at low chamber RH (less than 10%) to reduce the formation of HNO₃ (from heterogeneous hydrolysis of N₂O₅). From Fig.1 there is a spike in inorganic nitrate at the same time SOA increases. How do they know the SOA growth is not from partitioning of inorganic nitrates? The authors mentioned the use of SMPS, but they did not present any SMPS data. Did they see growth in SMPS, and how does that compare to the AMS data?

3a. Page 8863, line 5. In this study they used O₃+NO₂ to make NO₃. They should explain in more detail how they determined the relative importance of reaction with NO₃ vs O₃. Although isoprene+O₃ is not expected to make much SOA (Kleindienst et al., 2007), the first-generation products can react with ozone. This reaction is included in the study (Table 1, reaction 9) and the authors assumed a reaction rate for it (Page 8864, line 28). It seems to me that the % of first-generation products reacting with O₃ can be significant, depending on their choice of reaction rates. How would this affect their conclusions? If a lot of first-generation products react with O₃, perhaps that would help to explain why the measured nitrate:organic is not as high as they thought it should be?

b. Isoprene-O₃ reaction has an OH yield of about 0.19-0.27 (Finlayson-Pitts and Pitts, 2000). In this study CO is used as the OH scavenger. Using CO as OH scavenger produces the most HO₂ (compared to other OH scavengers, see Keywood et al., 2004). How does this affect the radical chemistry in the system and conclusions of this study? Is the HO₂ produced from the CO scavenger taken into account in the model?

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4. Page 8870, line 18. This sentence sounds misleading. It is not clear to me why “this would contradict the findings of Ng et al. (2008)...”. In Ng et al. (2008) we reported a series of SOA products (organic nitrates and peroxides) identified by the UPLC/(-)ESI-TOFMS and the mechanisms for the formation of these products are proposed. We did not suggest or imply these compounds are the only compounds present in the SOA and rule out all other SOA formation routes. Although most of the compounds have more than 1 nitrogen and we only detected one compound with 1 nitrogen atom, we did not make a strong statement that the SOA products must have at least 2 nitrogen atoms and imply a high nitrate:organic ratio. In Ng et al. (2008), we have emphasized that although a wide array of peroxides (with nitrate groups) is detected in the aerosol composition, there are large uncertainties associated with the quantification of peroxides owing to the lack of authentic standards. The authors should be clearer when they compared results to previous work to avoid misunderstanding/misinterpretation of previous studies.

5. Page 8871, line 15. Does the “extra” HO₂ produced from the CO scavenger play a role in that HO₂ dominates the fate of peroxy radicals? The authors suggested that “Ng et al. (2008) conducted a chamber study with higher total radical concentrations, but presumably similar ratios between HO₂ and RO₂”. With the CO scavenger chemistry, is it possible that HO₂/RO₂ ratio in this study is higher than Ng et al (2008)? If RO₂+HO₂ is more important here, the compounds formed may not be as “nitrated” as those in Ng et al. (2008). Perhaps this could also be one of the reasons that the nitrate:organic ratio is not as high as they would have expected?

6. Page 8872, line 3. In Figure 1, is there any AMS data before ~7:30am? The organics and nitrate signals are non-zero at the beginning of the experiment, why? Is this the “background” aerosol? The authors need to clarify this as the SOA growth they observed later is roughly in the same range as this “background”.

7. Page 8872, line 9. The authors need to explain how they corrected for particle wall loss. Wall loss is always a concern for chamber experiments, and it is particularly

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important in this case because the authors are interpreting SOA growth data that is presumably in the same order of magnitude as the wall loss.

8. Page 8872, line 13. Regarding the second period of growth (14:30-16:15), the authors wrote “the rapid growth of SOA observed is uniquely in the presence of high NO₃ concentration indicated that SOA formation was initiated by NO₃ oxidation rather than O₃”. They should perform some calculations to support this. Also, what about the first period (08:00-14:30)? (At the beginning of the experiment O₃ is added to initiate the production of NO₃. The reaction rate of NO₂+O₃ (at 298K) is 3.2e-17 cm³ molecule⁻¹ s⁻¹ (Seinfeld and Pandis) and the reaction rate of isoprene+O₃ is 1.3e-17 cm³ molecule⁻¹ s⁻¹ (Atkinson and Arey, 2003), it seems it is very possible that isoprene reacts mainly with O₃). It would be clearer if the authors could include a figure showing the relative importance of isoprene+O₃ and isoprene+NO₃ reaction over the course of the experiment.

9. Page 8875 and 8876. The authors reported an AMS nitrate:organic ratio of 0.1.8. They should explain in more detail how the analysis is performed and the uncertainties associated.

a. As the authors pointed out, there can be chemically different fragments at the same nominal mass (NO⁺ and CH₂O⁺ at m/z 30). Is the signal to noise ratio in their data good enough to separate the different species at the same nominal mass unambiguously. What fraction of m/z 30 (and m/z 46, if there is any organic interference at m/z 46) is organics? Such information would be very useful and should be included in the discussion. Also, I assumed the authors used the W mode data, but please clarify.

b. What relative ionization efficiency (RIE) did they use for nitrate and organics? Did they simply use the typical RIE of nitrate (1.1) and organics (1.4)? If the organic nitrates fragments to RO and NO₂ at the vaporizer, then the use of these RIEs is reasonable; on the other hand if the species vaporize as RONO₂ and then fragment to RO and NO₂ after electron impact, then the nitrate and organic portions of the organic nitrates

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will be detected with the same RIE. While it is difficult to distinguish one from the other, these possibilities should be mentioned.

c. Organic vs inorganic nitrate. It appears that the authors took as a fact that the “nitrate” measured by the AMS as organic nitrate. How can they be so sure? Are there other measurements of particle-phase organic nitrate or inorganic nitrate (with other instruments)? Did the authors look at the ammonium balance (is the ammonium that is measured in the particulate phase completely neutralized by the measured inorganic sulfate or is there an “excess” ammonium concentration that is indicative of possible neutralization in the form of inorganic nitrate? What is the NO_3^- to NO_2^- ratio and how does it compare to that observed during NH_4NO_3 calibrations? The mass balance of ammonium ion and the NO_3^- to NO_2^- ratio may offer some hints whether organic nitrate is present. The authors should include such a discussion in the manuscript.

10. Page 8877. The isomerization pathway discussion. When I first read this paragraph I almost got the impression the authors are implying that this reaction may have been overlooked in Ng et al. (2008). I do not think that is what they mean, but perhaps the way the paragraph is written just gave the wrong impression. We did mention this isomerization step that leads to the formation of hydroxycarbonyl (Figure 11 of Ng et al), which is then further oxidized to give the SOA product $\text{C}_5\text{H}_9\text{NO}_7$ (Figure 17 of Ng et al). We found these products to be minor. If the authors suggest that the isomerization pathway might be significant, then they need to back that up with calculations and realistic estimates of rate constants. Also, in Figure 12, I think on the top branch it should be kO_2 instead of kdecomp ? In Ng et al. (2008) it is proposed that the further oxidation of hydroxycarbonyl may form the $\text{C}_5\text{H}_9\text{NO}_7$ product (the only particle-phase product detected with only 1 nitrogen atom), which is different from their second product. We did see their second product in our data (in CIMS), but it is a minor product and we did not detect this in the particle phase.

11. Page 8877. Second paragraph. I think the main point of this paragraph is that the AMS is measuring a much lower nitrate:organic ratio than one would expect from

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the structures of these products, so perhaps the organic nitrate content is underestimated by the AMS. But the way this paragraph is written it appears to say that in Ng et al. (2008) many highly “nitrated” species were detected and so this is inconsistent with their AMS data. As pointed out in comment 4, in Ng et al. (2008) we did not suggest the detection of highly nitrated species automatically imply that a high overall nitrate:organic ratio in the aerosols formed. We have emphasized the high uncertainties associated with the quantification of such species owing to the lack of authentic standards. I think it is a valid point that the nitrate content may have been underestimated based on AMS data, given the uncertainties associated. In Ng et al. (2008), the data were taken with a quad AMS. Since there is the possibility of organic interference at m/z 30, we could not unambiguously quantify the organic nitrate measured by the AMS. With these uncertainties, we did not feel we were able to use the AMS data in a quantitative way and hence such numbers were not reported. However, an HR AMS is employed in this study. With some detailed analyses of the AMS data, it may offer the authors a great opportunity to look into how organic nitrates may fragment in the AMS. And as mentioned before, more discussion should be included regarding these analyses.

12. In their experiment the initial isoprene concentration is lower than in Ng et al. (2008). Although radical chemistry is not modeled explicitly in Ng et al. (2008), is it possible that in their case RO_2+RO_2 is not occurring as much (and hence lower the “nitrate content” of the SOA products in their experiment)?

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