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

A. Rollins

ice@berkeley.edu

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Reviewer comment: 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 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?

Response: We describe one experiment on the isoprene + NO_3 system. This experiment was conducted during a series of other experiments all of which involved the same equipment and experimental procedures. The experiment produced a number of results that are consistent with previous work and there are a number of checks for internal consistency among the measurements, giving confidence that it would be reproducible should someone attempt it again.

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 HNO_3 (from heterogeneous hydrolysis of N_2O_5). 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?

Response: We conclude from observed NO_2^+/NO^+ ratios that the nitrate is from the SOA and not inorganic.

The measured SMPS mode diameter grew from initial 50 nm to 90 nm during the course of the experiment. A transmission efficiency of 1 was assumed through the aerodynamic lens of the AMS. The collection efficiency CE was assumed to be 0.5 for $(NH_4)_2SO_4$ and 1 for organics and nitrate. Under these assumptions AMS and SMPS agree well when deriving a mass loading from SMPS size distributions with a density of 1.4 for ammonium sulfate and 1.2 for the organic fraction.

3a. Page 8863, line 5. In this study they used O_3+NO_2 to make NO_3. They should explain in more detail how they determined the relative importance of reaction with NO_3 vs O_3. Although isoprene+O_3 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 O_3 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 O_3, perhaps that would help to explain why the measured nitrate:organic is not as high as they thought it should be?

Response: We calculate the relative importance O_3 vs NO_3 to the consumption of isoprene using reactions and rates included in MCM V3.1. To calculate the importance of O_3 to reaction with the first generation oxidation products, we used rate constants based on a structural analog (2-methyl-2-butene) with known O_3 and NO_3 rate constants.

Our conclusion that the majority of the SOA was from the reactions with NO_3 is based on the observation that SOA growth occurred only during the short period of time when the NO_3 concentration was high. This is shown in Figure 1. Panel f shows the AMS data for organic and nitrate aerosol, which increase only from 14:15-16:15 Hr concurrent with an increase in NO_3 concentration from 2-3 ppt before 14:15, up to 50-150 ppt. SOA production promptly stopped when the NO_3 concentration decreased back to <5 ppt at 16:15. During this same period, the O_3 concentration initially increased from 20 to 60 ppb by the addition of O_3 to the chamber, but there was no step change in the O_3 concentration occurring simultaneously when SOA production ceased.

b. Isoprene-O_3 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 HO_2 (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 HO_2 produced from the CO scavenger taken into account in the model?

Response: We used the MCM V3.1 to model the O_3 isoprene reaction and include OH + CO production of HO_2. In the MCM OH is produced with a 13.5% yield from this reaction. We calculate that $<10\%$ of the HO_2 produced in the chamber is from OH + CO, with the majority of it being from RO + O_2 reactions. If the OH yield were doubled to the maximum 27% described in Finlayson-Pitts and Pitts, RO + O_2 would still be the dominant source of HO_2.

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/(-)ESITOFMS 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.

Response: Our apologies. Your analysis was thorough and we overlooked the possibility that species contributing the majority of the aerosol mass were unidentified. Text suggesting that our findings are contradictory will be removed from the manuscript.

5. Page 8871, line 15. Does the "extra" HO_2 produced from the CO scavenger play a role in that HO_2 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 HO_2 and RO_2". With the CO scavenger chemistry, is it possible that HO_2/RO_2 ratio in this study is higher than Ng et al (2008)? If RO_2+HO_2 is more important here, the compounds formed may not as 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?

Response: This question is addressed in the response to 3b.

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".

AMS data of the empty chamber was taken. We thank the reviewer for pointing out the missing values and added the data accordingly. The zero measurements showed values of 0.012 ± 0.023 (NH_4), 0.007 ± 0.005 (NO_3), 0.003 ± 0.033 (Org) and -7.4 $\times 10^{-5}$ ± 0.002 (SO_4). We assume that the very minor (0.2 μg/m^3 for organics and 0.02μg/m^3 for nitrate) signals come from impurities in the ammonium sulfate or from uptake in the chamber. Note that after the addition of ammonium sulfate seed aerosol NO_2, CO and Isoprene were added to the chamber consecutively. None of the gas additions changed the relative abundance of organics or nitrate in the aerosol significantly. We therefore conclude that the observed organics and nitrate are not a consequence of addition of the gases. See additional Figure 1.

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 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.

Response: We wrote, "We assume that the observed SOA is due the combined effects of SOA production and wall loss and in Fig. 7 we show the SOA corrected for this loss."

By this we meant that between any two AMS data points the observed change in OA ($Delta$OA) was due to production (P) - wall loss (L) where the wall loss term is an exponential decay with a 3.7 hour lifetime (L = OA * exp(-Δt / 3.7hrs)). Rearranging we can calculate the production term alone at each time step (P = ΔOA + OA * exp(-Δt / 3.7hrs) = OA * (1+exp(-Δt / 3.7hrs)). The observations were then used to calculate the production, and the net production at each time step is summed to arrive at a dilution correction.

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 NO_3 concentration indicated that SOA formation was initiated by NO_3 oxidation rather than O_3". 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 NO_2+O_3 (at 298K) is 3.2e-17 cm^3 molecule^{-1} s^{-1} (Seinfeld and Pandis) and the reaction rate of isoprene+O_3 is 1.3e-17 cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003), it seems it is very possible that isoprene reacts mainly with O_3). It would be clearer if the authors could include a figure showing the relative importance of isoprene+O_3 and isoprene+NO_3 reaction over the course of the experiment.

Response: Box model calculations using these rate constants show the NO_3 chemistry to be 80% or more of the isoprene loss. See additional Figure 2.

9. Page 8875 and 8876. The authors reported an AMS nitrate:organic ratio of 0.18. They should explain in more detail how the analysis is performed and the uncertainties associated.

Response: As described in Fry et al. the aerosol nitrate was quantified by adding the NO^+ and NO_2^+ signals as determined in the HR mode of operation of the AMS. Organic ions present at the same nominal mass as nitrate peaks were corrected for. The NO_2^+/NO^+ ratio observed in the isoprene + NO_3 SOA is considerably lower (0.16) than what is typically observed for NH_4NO_3 aerosol (0.35). This is taken as indication that the nitrate observed is not formed from inorganic nitrate uptake but is organic nitrate.

a. As the authors pointed out, there can be chemically different fragments at the same nominal mass (NO^+ and CH_2O^+ 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.

Response: The signal to noise at m/z 30 was high enough to unambiguously separate and identify the NO^+ and CH_2O^+ ion signals. The fractional abundance of CH_2O^+ was 10% of the NO^+ ion. No significant organic interference at m/z 46 was observed. The AMS W mode was used.

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 NO_2 at the vaporizer, then the use of these RIEs is

reasonable; on the other hand if the species vaporize as $RONO_2$ and then fragment to RO and NO_2 after electron impact, then the nitrate and organic portions of the organic nitrates will be detected with the same RIE. While it is difficult to distinguish one from the other, these possibilities should be mentioned.

Response: As mentioned we assume that the vaporization of the thermally unstable organic nitrates leads to a fragmentation into RO + NO_2. Therefore we performed our data analysis with RIE of 1.1 for NO_3 and 1.4 for the organics. However the RIE for nitrates which is measured on ammonium nitrate is not necessarily the same RIE that should be used for NO_2, and this difference may contribute to the discrepancy.

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^+ 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^+ to NO_2^+ ratio may offer some hints whether organic nitrate is present. The authors should include such a discussion in the manuscript.

Response: Interpretation as organic nitrate followed the same reasoning as described in Fry et al. There are two pieces of evidence pointing to the nitrate being organic nitrate. First the NO_2^+/NO^+ ratio was observed to be significantly lower for the nitrate measured here than for NH_4NO_3 used for calibrations. Secondly, when considering the ammonium balance the whole ammonium measured can be explained by $(NH_4)_2SO_4$ seed aerosol. Adding NH_4 to neutralize inorganic NO_3 would increase the NH_4 above the measured level for the period of second organic and nitrate increase (after 14:20).

While the difference is small it is clearly observed (see figure above).

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 $C_5H_9NO_7$ (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 $C_5H_9NO_7$ 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.

Response: We do not mean to suggest anyone overlooked something. Atkinson et al. (2007) recommend rate constants for the relative importance of alkoxy isomerization vs reaction with O_2. For primary alkoxy radicals which we expect from the isoprene + NO_3 reaction, a rate constant at 298K O_2 of 9 $\times 10^{-15}$ cm^3/molecules/s is recommended, so with 21% oxygen, k $\times$ [O_2] = 4.6 $\times 10^4$ s^-1. The recommendation for isomerization by abstraction of a primary hydrogen atom at 298K of 3.2$\times 10^5$ s^{-1}. Comparing these reaction rates suggests that the isomerization pathway could be almost 7 times as fast as reaction with O_2.

Thank you for catching our error in Figure 12.

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 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.

Response: As stated previously, we will remove the discussion of your data as evidence that the AMS may detect N in organic nitrates with reduced efficiency relative to inorganic.

No mixed organic/N ions could be identified in the HR mode. Organic nitrate was thus quantified based on the identified NO^+ and NO_2^+ ions. As in Fry et al. we conclude that the major signal from organic nitrates is observed at m/z 30 (NO^+) and 46 (NO_2^+) in the AMS. The deviation from the fragmentation pattern typically observed for inorganic nitrates offers an indicator for the presence of organic nitrates. The following sentence is added to the manuscript:

"As previously reported for the NO_3 oxidation of b-pinene (Fry et al. 2009) the AMS measures organic nitrates as signals on m/z 30 and 46 mainly. In contrast to inorganic nitrate which is characterized by a ratio R of NO_2^+/NO^+ of 0.35 we find an R of 0.16 for the organic nitrate."

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)?

Response: It is possible that RO_2 + HO_2 was more important in these experiments than in those of Ng et al. We do not attempt to reanalyze the data of Ng et al. to estimate the RO_2 + RO_2 vs. RO_2 + HO_2 reaction rates. However, we presume that the relative concentrations of RO_2 and HO_2 would be similar in the two experiments.

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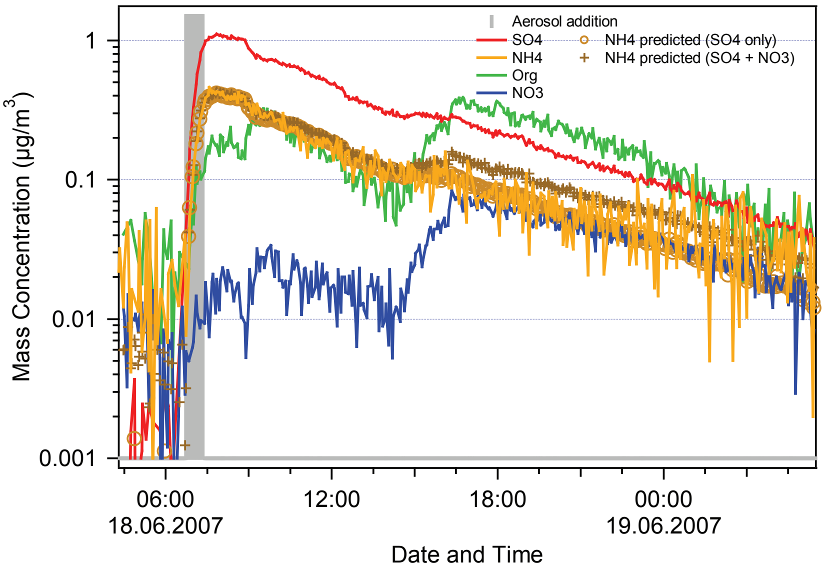

Fig. 1.

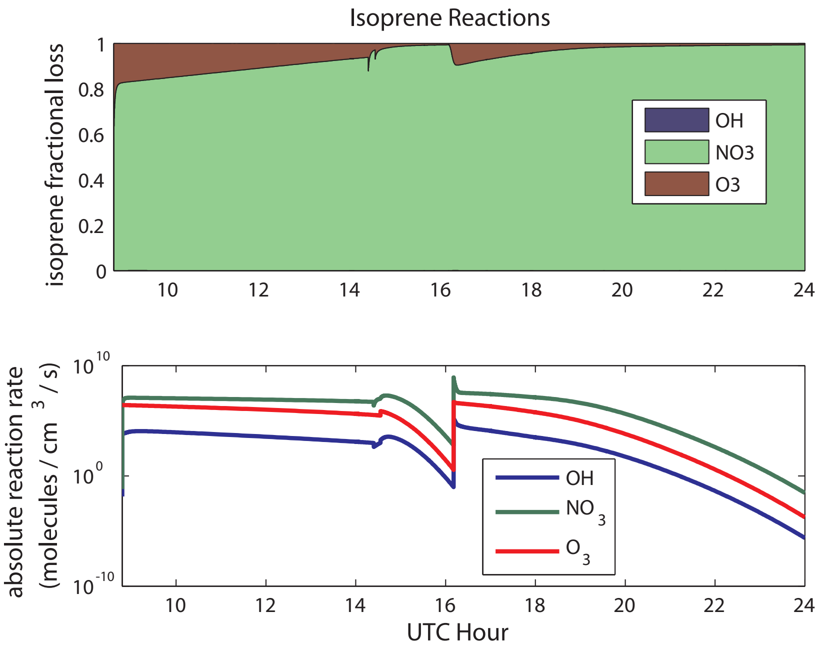
Isoprene Reactions
isoprene fractional loss
1
0.8
0.6
0.4
0.2
0
10
12
14
16
18
20
22
24
OH
NO3
O3
absolute reaction rate (molecules / cm 3 / s)
10 10
10 0
10 -10
10
12
14
16
18
20
22
24
UTC Hour
OH
NO 3
O 3

Fig. 2.