

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

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Reviewer comment: This manuscript presents the results of one day of experiments in an outdoor smog chamber, focusing on the oxidation of isoprene by nitrate radicals. The results are indeed interesting and highlight the fact that second generation products likely dominate the SOA yields. The experiments were carefully performed under somewhat realistic conditions, and the interpretation of the results is fairly sound. Under some circumstances, the authors may be attempting to be more quantitative than is possible with the current results and associated uncertainties. The biggest issue is the use of the AMS data without clearly stating the associated uncertainties or calculation methods. This paper can be improved with a number of changes and clarifications throughout, which are outlined below.

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Response: We will add details of the AMS data analysis to the manuscript.

Pg 8860 line 19: how much lower is the NO_x and isoprene compared to others? Is it 15% or orders of magnitude? This will strengthen the argument that the experiments were done under realistic conditions.

Response: The experiment was initiated with 9.6 ppb isoprene and 16 ppb NO₂, and the measured NO₃ concentration during the isoprene consumption was ≈2 ppt. The lowest reactant concentrations reported in previous experiments were that of Ng et al. 2008, which was 18.4 ppb isoprene. In the Ng et al. experiment N₂O₅ was added directly to the chamber and they report calculating for one of their yield experiments that the resulting NO₃ concentration was ≈140 ppt.

Pg 8863, line 1-3: Do the authors mean that the concentration in the chamber was increased to 23 and 43 ppb? Or that they added 23 ppb? The figures imply the former, but clarify anyway.

Response: The concentrations of NO₂ and O₃ were increased by adding an additional 23 ppb and 43 ppb respectively. This can be seen in Figure 1a.

pg 8865, line 24: The associated figure does not show any NO₃ available at all, probably because the scale should be adjusted.

Response: We will adjust the scale in the revised manuscript.

Pg 8866: A number of estimates are made here of the importance of certain reaction channels. It is not clear, at least at this point, how these estimates are derived.

Response: The estimates made here regarding the importance of e.g. isoprene + NO₃ reaction vs. isoprene + O₃ reaction, or RO₂ reaction partner are results of

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model calculations which are described in the following section. We will add text which explains pointing out that details of the model appear in subsequent sections of the paper. We chose to give this description of the different time periods in the experiment before we discuss the model, so that it is clear to the reader why different parts of the experiment are used as constraints on different model parameters.

Line 6- 7: how do you know that the initial oxidation products are the important sink? Be clear on how this is determined.

Response: The concentrations of NO_3 and N_2O_5 were observed in multiple separate VOC free experiments. These experiments were accurately modeled with NO_x/O_3 chemistry and a single wall loss rate. That wall loss was small compared to the total loss rate of NO_3 observed in this experiment implying that the presence of organic compounds here is the source of the losses. As the chemistry of isoprene+ NO_3 is well known, we conclude that some products of the isoprene oxidation are responsible for the model /data mismatch that results if we don't include the additional chemistry. We will add text describing these facts and the analysis of the VOC free experiments.

Line 12: "11 ppb was added" should be something like "the chamber concentration was 11 ppb"

Response: This text now reads ". . .additional isoprene was added to the chamber, bringing the concentration to 11 ppb."

Line 9: By "VOCs" do the authors mean MVK and MACR? If so then say this. Also, MVK and MACR do not seem to be accumulating any more rapidly than before in the figure. Perhaps this should be clarified in the figure.

Response: MVK and MACR are generated by reacting one double bond of isoprene. Here we are saying that the second generation oxidation products accumulated, which would not have been MVK or MACR. By "VOCs" we mean any compounds which

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would be generated by the reaction of NO_3 with the initial oxidation products. We did not measure specific compounds and therefore cannot name them. We will reword this sentence to be clearer about this. It now reads:

"Second generation oxidation products rapidly accumulated through the reaction of NO_3 with the initial isoprene oxidation products."

Pg 8866, line 26: This is a "measured" branching ratio from what I can tell from the following discussion, but it is in the "model optimization" section. Perhaps clarify that it is measured.

Response: This quantity was determined by optimizing the model, as is described in the discussion on page 8867. P8867 line 22-23 state that it was determined in this way.

Pg 8867, line7: According to eq. 1 delta isoprene is what is required for the branching ratio. Why not just use the measured isoprene instead of NO_3 ? Presumably the O_3 oxidation of isoprene is small relative the other NO_3 channels.

Response: For this second addition of isoprene to the chamber the amount of isoprene injected and consumed immediately was not known with enough precision to determine the branching ratio in this way. The time scales for the chamber mixing and consumption of isoprene were comparable, such that the PTR-MS did not get an accurate measurement of the total amount of isoprene added to the chamber. This can be observed in Figure 1. Fig 1c shows that ≈ 1.5 ppb $\text{NO}_3 + \text{N}_2\text{O}_5$ were immediately (within 5 minutes) consumed when the isoprene was added, but no corresponding stepwise decrease in the measured isoprene (Figure 1 e) is observable.

The noise in the PTR-MS also obscures any fast change of isoprene over this short time. For example, at the beginning of the experiment (8:00) when isoprene concentration is high and relatively steady, for 5 minutes of averaging the mean and standard deviation are 9.4 ± 0.4 ppb, which is about 4%. Subtracting two numbers of

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this order, each with error (i.e. 11 ± 0.4 and 9.5 ± 0.4) yields a large uncertainty in the difference. This could also be why a negative step change in the measured isoprene is not observable.

Pg 8868, line 11-14: These lines are not clear. A "positive bias" for what?

Response: We mean that in this case the modeled NO_2 is significantly greater than the measurements. This text now reads "We note that a yield of greater than 0% for NO_2 results in modeled NO_2 which is significantly greater than the measurements."

Pg 8869, line 2-3: this was stated already in the previous few lines.

Response: In the previous paragraph we compare our observations of organic nitrate formation to previous studies. Here we discussing MVK, MACR and MEK in the context of previous studies, and this was not stated previously.

Pg 8869, line 23-29: "does not reappear": does this mean it has formed nitric acid (HNO_3) which is not measured? I assume that abstraction of an aldehydic group would make HNO_3 . From which molecule? Reference to a molecule in a figure would be useful. If you are making nitric acid, does any of it end up in the aerosol? This should be measurable with the AMS.

Response: Yes, we assume that HNO_3 was formed from the reaction of aldehydes with NO_3 , although HNO_3 measurements were not available. The carbonyl-nitrate which is the highest yield product of the isoprene + NO_3 reaction (Fig 2) is an aldehyde.

The AMS measures nitrate on m/z 30 (NO^+) and m/z 46 (NO_2^+). Inorganic nitrate such as from NH_4NO_3 is characterized by a ratio of $\text{NO}_2^+/\text{NO}^+$ of 0.35. In the experiment described we found a much lower ratio of 0.156 throughout the experiment which is taken as indication of organic nitrate. We conclude that no significant HNO_3 uptake or heterogeneous N_2O_5 hydrolysis is observed in isoprene NO_3 SOA at the conditions in

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the chamber.

Pg 8870, line 1 -19: MBO is not really very similar to hydroxyl nitrate since it has no nitrate groups. It would be difficult to make any conclusive arguments from this comparison given the admitted uncertainties. If it a very rough calculation then in my opinion the paragraph adds little to the paper and can be removed.

Response: To our knowledge, rate constants for the reactions of NO_3 with beta-substituted alkenes have not been reported. However, NO_3 and OH have been shown to have similar trends in reaction rate constants towards alkenes, as is expected due to their similar reaction mechanisms. For OH, it has been shown that the substitution of a nitrate group on the carbon beta to an alkene group reduces the rate constant toward the double bond by about a factor of 1/2, and beta substitutions in general have a much smaller effect than the number of alkyl substitutions to the double bond itself. Therefore, we thought that MBO was a reasonable molecule to use for an order of magnitude comparison. Here we only present the information that is known for the reader to consider, and to put the reaction rate we calculate in context of the existing literature.

Pg 8871: These paragraphs describing the fate of peroxy radicals seems misplaced and unnecessary. That is not the focus of the paper, and cannot be satisfactorily answered anyway with the data that is presented. I would recommend removing this discussion.

Response: We believe it is important to retain discussion of peroxy radical chemistry because differences in peroxy radical chemistry are believed to be one of the primary reasons that similar experiments can produce different product and aerosol yields, and because it is that fate of peroxy radicals that will determine how well a chamber experiment mimics the atmosphere. Failure to discuss these issues in other papers tends to obscure the importance of peroxy radical fate and our ability to evaluate whether a given experiment is directly relevant to the atmosphere.

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Pg 8872, line 9: How was the SOA corrected for wall losses? Using the number density change?

Response: Yes. A fan was used in the chamber, mixing gasses and particles continuously. The size dependent particle loss correction which is typically applied to data from chamber SOA experiments was not required because this rapid mixing made size dependent diffusion losses irrelevant.

Pg 8872, line 12-13: Initiation by NO_3 or O_3 would depend on the reaction rates I presume. There needs to be more clear evidence that this is indeed the case, especially since AMS results later in the paper tend to show the opposite result.

Response: We agree that the oxidation of the first generation oxidation products and subsequent production of SOA will be determined by the reaction rate constants for these compounds towards NO_3 and O_3 . We also presume that the rate of oxidation will be proportional to the concentration of the oxidant, i.e. $[\text{NO}_3]$ and $[\text{O}_3]$. We observed an increase in SOA when the concentration of NO_3 increased, while $[\text{O}_3]$ remained relatively constant, and therefore find this as sufficient evidence that the reaction which caused the SOA formation was the reaction with NO_3 .

We disagree that AMS results show the opposite. The only observation we make is, that the AMS does not show the high nitrate content that would be suggested when assuming SOA is exclusively composed of the nitrates given in figure 9. However, as discussed the AMS has not been calibrated on organic nitrate aerosol, and therefore the accuracy of aerosol nitrate calculated in this way is unknown.

Pg 8873, Line 3: $12.5 \mu\text{g}/\text{m}^3$ is not clear from the figure. Are they including what occurred before 10? Or only between 10-14?

Response: Yes, we are describing the total amount of isoprene reacted, which is

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indicated on the blue axis.

Pg 8873, Line 1-20: this paragraph is somewhat unclear. It should be clarified here why the 1st generation yield was calculated from 14Hr but 2nd generation from the whole day. Also, comparing AMS data to the modeled results is somewhat dangerous. There is no mention of the collection efficiency (CE) or transmission efficiency (TE) associated with the AMS. This will drastically change the amount of mass measured and the yield determined. What sizes were the particles? Some of them may not make through the AMS at all, this should be considered also. A discussion of the CE used if any should be included in the discussion here. Also, does the TD-LIF also measure inorganic nitrates? Since the AMS will. It is not clear at this point how the AMS organic nitrate is calculated, ie: from what mz's, including inorganic nitrate or not? All this needs to be considered and clarified in this paragraph before one can truly make any statements about yields.

Response: The SOA yield from first generation products was calculated as the amount from 14Hr because we calculate that at this point in the experiment a minimal amount of the second generation products had been formed. Thus, at this point any SOA would be from first generation products only. After this time we believe based on our modeling that the production of second generation products was rapid, and we observe that the formation of these products is well correlated with SOA formation. Thus, we calculate the SOA yield from these products as the SOA increase after this point.

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 $(\text{NH}_4)_2\text{SO}_4$ 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.

TD-LIF only measures organic nitrates.

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AMS organic nitrate is calculated based on the observed signals on m/z 30 and 46. It is assumed at this point that the Relative Ionization Efficiency (RIE) for the nitrate is 1.1. The signal at m/z 30 was observed to contain NO^+ and CH_2O^+ . The organic ion contribution was subtracted from the total m/z 30 signal for nitrate quantification. No significant contribution of organic ions was observed at m/z 46. The total signal at this m/z was attributed to NO_2^+ and thus considered as nitrate. The observed $\text{NO}_2^+/\text{NO}^+$ ratio was 0.16 which is significantly lower than the ratio of 0.35 observed for NH_4NO_3 aerosol.

No signals of mixed organic and nitrate containing peaks were detected. From the observed $\text{NO}_2^+/\text{NO}^+$ ratio we conclude that inorganic nitrate was not contributing significantly to the observed nitrate signal.

Pg 8874, line 11: do the authors mean "lower" instead of higher? What is the potential range of vapour pressures for the 2nd generation products? Are they all quite similar?

Response: We mean higher. Carbonyls are generally observed to be more volatile than alcohols. We calculated vapor pressures for the group of second generation products shown in Figure 9 using the method of Pankow and Asher. Replacing an alcohol group with a carbonyl group in each molecule and repeating the calculation results in a factor of 6-8 increase in the vapor pressure for the suite of compounds.

Pg 8874, line 18: where does $0.6 \mu\text{g}/\text{m}^3$ come from?

Response: This was the amount of OA observed without correcting for dilution (Figure 1f), which should be used for the partitioning calculation. We will add a reference to Figure 1 in the text.

Pg 8875, line 1-23: The calculation on this page are quite uncertain it would seem. I am not sure much of a conclusion can be reached when one considers the

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range of products formed, the uncertainties in vapour pressures, the assumptions of activity coefficients, and the MWom assumed. The authors should be very careful to not get carried away with what can actually be concluded here. It would make things somewhat clearer if figure 10 could include other conditions ie: vapour pressures etc. . . which could constrain their estimates and make it at least visually clearer what the "range" of their data actually is.

Response: Here we are attempting only to demonstrate that our observations are reasonably consistent with SOA formed by equilibrium partitioning of second generation C5 compounds, and inconsistent with SOA formation from first generation C5 products, or C10 second generation products. This is done under the guise of making typical assumptions about activity and MWom. The associated uncertainties in calculating the expected SOA yields from different compounds are indeed significant. Further, as the reviewer notes we are attempting to quantify a yield by comparing a model calculation of the amount of precursor reacted, which was not directly measured, to the dilution corrected SOA production. These calculations also include uncertainties.

One goal here was to consider how well a semi-explicit model might capture the SOA formed from multiple generations of isoprene oxidation, if SOA is calculated through equilibrium partitioning of compounds using typical tools for calculating vapor pressures and making the typical assumptions about activity and MWom. We found that in doing this calculation one finds the first generation products too volatile to produce SOA, and the second generation products produce the right order of magnitude of SOA to reproduce our data.

Pg 8876, line 1: 0.18 and 0.2 are probably not statistically different from each other.

Response: Agreed, we will note that in the text.

Pg 8876, line 8: Which efficiency are they referring to? IE, CE or TE?

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Response: Here we are referring to the observed total concentration detection efficiency, which in principle could be due to a reduced IE, CE or TE for organic nitrate relative to the ammonium nitrate calibration standard. We are not in a position to say anything other than the product of $IE \times CE \times TE$ would be reduced.

Pg 8876, line 12: how do they get 0.66 from 1.05? In any case Fig 9 shows that it was 1.2 not 1.05. It is also important that the authors clarify how the AMS organic nitrate is calculated. Doing so is not a trivial task, and it may not surprising that the mass ratios are so small given all the issues with calculating such. Did the authors include organic nitrogen buried in the organic m/z's? This could well be a significant portion, and should be possible to determine given that they are using a high-res instrument. Did the authors simply use the AMS reported NO_3 signal or did they dig a bit deeper? What about inorganic nitrate? What contribution does it have to the NO_3 signal if at all? A more detailed explanation of how the AMS numbers are derived would be very useful.

Response: We will clarify with math in the text how we believe the decomposition of organic nitrates on the heater would cause these numbers to change. In general, because the nitrate group is a large fraction of the mass, whether this is included in the organic mass or not makes a large difference. Other questions about the AMS data analysis are addressed above and will also be clarified in the instrumentation section of the paper.

Figure 1: more x-axis tick labels would be nice, and VOCs on the right axis would help clarity.

Figure 5: Instead of showing the model-data difference, a direct comparison of the data would be easier to visualize.

Figure 7 and 8: x-axis title needed.

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Technical corrections: Pg 8866, line 21: "pervious" to "previous" Pg 8870, line 13: too many uses of the word "only". Pg 8873, line 4: "pervious" to "previous"

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 8857, 2009.

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