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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.

Anonymous Referee #3

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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.

Pg 8860 line 19: how much lower is the NOx 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

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.

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

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. Line 6-7: how do you know that the initial oxidation products are the important sink? Be clear on how this is determined. Line 12: "11 ppb was added" should be something like "the chamber concentration was 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.

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.

Pg 8867, line 7: According to eq 1 delta isoprene is what is required for the branching ratio. Why not just use the measured isoprene instead of NO₃? Presumably the O₃ oxidation of isoprene is small relative the other NO₃ channels.

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

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

Pg 8869, line 23-29: "does not reappear": does this mean it has formed nitric acid (HNO₃) which is not measured? I assume that abstraction of an aldehydic group would make HNO₃. 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

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be measurable with the AMS.

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.

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.

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

Pg 8872, line 12-13: Initiation by NO₃ or O₃ 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.

Pg 8873, Line 3: 12.5 ug/m³ is not clear from the figure. Are they including what occurred before 10? Or only between 10-14?

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

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needs to be considered and clarified in this paragraph before one can truly make any statements about yields.

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?

Pg 8874, line 18: where does 0.6 ug/m³ come from?

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 range of products formed, the uncertainties in vapour pressures, the assumptions of activity coefficients, and the MW_{OM} 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.

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

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

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 NO₃ signal or did they dig a bit deeper? What about inorganic nitrate? What contribution does it have to the NO₃ signal if at all? A more detailed explanation of how the AMS numbers are derived would be very useful.

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

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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.

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”

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

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