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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.

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Reviewer comment: The paper presents significant and interesting experimental and model simulation results on isoprene chemistry. The importance of the second generation oxidation products of isoprene are emphasized and well supported. The paper includes important comparisons to some recent work by other groups, although in some cases the comparisons seem to imply inconsistencies without actually specifying what they are. The paper could be improved with minor changes including adding more detail for the sake of clarity and expanding the experimental explanations to strengthen the results found.

Page 8858 Line 3. The acronym SAPHIR should be defined. Line 9. Briefly mention more conditions of the 16 hr experiment. What was the temperature in the chamber?

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Were the nitrates levels high, low?

Response: Additional text will be added to spell out SAPHIR. The temperature varied from 289K to 301K throughout the day and the organic nitrate observations peaked at 7.8 ppb. Additional text will be added to the abstract to better describe the experimental conditions.

Page 8859 Line 1. Word choice? "Traditionally"

Response: The text now reads "... typically..."

Line 11. An example of a location where high NO_x levels and isoprene sources are collocated would be expected, would add nicely.

Response: The text now reads "...collocated with isoprene sources such as the northeast U.S or any city, or power plant surrounded by forests..."

Line 17 and 21. Specify if these two studies were conducted in chambers.

Response: Both were chamber studies, and this will be noted in the text.

Line 27. Clarify; is the second step the oxidation at the second double bond?

Response: We believe based on the products that have been observed in aerosol that some of the initial oxidation products react at the remaining double bond, but some are aldehydes that react by abstraction of the aldehydic hydrogen. We will amend the text to read "There is little detailed information about the fate of the initial oxidation products, which are primarily alkenes and aldehydes. Both functional groups may have important roles in the reactivity."

Line 19. Perhaps include the lower levels used in the experiment are more relevant to the actual atmosphere. Do the "prior experiments" include Ng et al. (2008)?

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Give specific references lest the reader fail to value the prior work appropriately.

Response: The text now reads. . . "In this experiment we report a chamber experiment on the reaction of isoprene with NO_3 , performed under conditions of isoprene (max 11 ppb) O_3 (max 62.4) and NO_x (max 31.1), where NO_3 is generated in situ via the reaction of $\text{O}_3 + \text{NO}_2$. To date, the isoprene + NO_3 experiment with the lowest reported reactant concentrations is that of Ng et al. (2008) who used a lower limit of 18.4 ppb isoprene and added N_2O_5 directly to the chamber."

Page 8861 "the NOAA group" is an imprecise term which would be somewhat akin statistically to saying "the German group," and which could refer to thousands of groups at dozens of NOAA facilities - doing a disservice to the scientists involved. For the purposes of accuracy and posterity, perhaps "Ravishankara and coworkers" is meant?

Response: The text now reads "Brown and coworkers."

Page 8862 Line 13. Specify the AMS measured non-refractory aerosol chemical.

Response: In the SAPHIR chamber the aerosol sources are well known and consist of aerosol from the aerosol generator used to supply the ammonium sulfate seed aerosol and of secondary formation of aerosol. The wording is changed according to the suggestion and now reads: "... was operated to measure the non-refractory aerosol chemical composition. . . ."

Page 8863 Line 5. With which instruments was it determined $\approx 90\%$ of the isoprene reacted with NO_3 and $\approx 10\%$ with O_3 ?

Response: The relative consumption of the isoprene was calculated with the chemical kinetics box model based on the MCM V3.1 and is described in the manuscript.

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Measurements of O₃ (CL), NO₃ (CaRDS) and isoprene (PTR-MS) matched the model well enough to be certain of the importance of these isoprene sinks.

Line 8. Were losses to the chamber walls considered?

Response: Yes, these are mentioned later on page 8866. We will move this sentence up to page 8863.

Page 8864 Line 1. Were the conditions of Kwok et al., 1996's work similar to the ones used here?

Response: The conditions in the experiment of Kwok et al. were significantly different from those in this study. We initially added 9.6 ppb isoprene, 16 ppb NO₂ and 37 ppb O₃ resulting in the slow consumption of isoprene which was limited by the NO₂ + O₃ → NO₃ reaction. Kwok et al. added 0.5 - 1.0 ppm N₂O₅ to a chamber which was initially filled with 1.0 - 2.0 ppm isoprene, thus resulting in an immediate consumption in the isoprene. However, the yield to form MVK and MACR is determined primarily by the positions at which NO₃ and then O₂ add onto isoprene to form a specific peroxy radical conformer. Thus, we should not expect significantly different yields from the different experiments. The yields reported by Kwok et al. are in good agreement with our observations, and we discuss this chemistry on page 8869.

Page 8866 General comment Gas phase products. Use a more descriptive title for the three time periods that refers to the chemistry that dominated in addition to the time period. What were the light conditions during the experiment? Was the amount of light varied to simulate an actual 16 hr period by keeping the shuttering open in the aluminum structure? Also; change "pervious" to "previous"

Response: The experiment was conducted completely in the dark.

Page 8868 Line 21. A table summarizing the experiments conducted at different

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concentrations of isoprene would strengthen the statement high yields of alkyl nitrates is robust.

Response: This table will be added.

Page 8869 Line 16. Perhaps mention some other measurements in your experiment that co-occurred with this surprisingly high concentration of MEK, so the reader can better understand the environment this occurred in.

Response: All the other available measurements are described in the text.

Line 25 The uncertainty on the "about 40%" and "about 60%" should be clearly stated.

Response: We previously stated this as 40 ± 20 and 60 ± 20 . We will change the text in this sentence as well.

Page 8870 Line 13. Typo? Multiple "only"s. However, this would contradict the findings of Ng et al. (2008) who report at least 2 nitrogen atoms in almost all of the molecules forming SOA from this system." This statement seems to imply that Ng claimed a minimum ("contradict"; "at least") were required; my reading of their work was simply that they did not identify single-nitrogen compounds - not that they claimed they did not exist. I suggest the authors give careful consideration to how they represent their competitors' work, so as to minimize publication of misleading information. Perhaps they should consider whether their findings might more properly "supplement" or "expand" the earlier work, which would show their contribution while not causing misinterpretation of earlier work.

Response: Thank you for pointing out our misleading citation of the work by Ng et al. We will rephrase this section to make this important distinction clear, and more accurately describe their work.

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Page 8871 Line 26. How your experiment addresses alcohols. "then" instead of "than" is meant?

Response: We have no measurements of whether oxidation products contained alcohol, carbonyl, or hydroperoxyl functionality. However, other chamber studies which have observed specific oxidation products such as the C5 hydroxynitrate and C5 carbonylnitrate have observed the carbonylnitrate as the dominant product, with hydroxynitrate $\approx 1/5$ as much, and hydroperoxide-nitrate even less. Since these studies did not report model calculations of the different products and HO₂ would have been generated with the same yield from isoprene oxidation in all experiments, we report the discrepancy here.

Page 8872 Line 14. Interesting and well-written statement. Line 16. Provide a sense of the time lag between peaks in isoprene concentrations and SOA concentrations. How do you think this time lag might change for observations in an ambient environment?

Response: We observed no SOA growth until the isoprene concentration was below ≈ 2 ppb. We expect that in an ambient environment isoprene concentrations near this will also inhibit the NO₃ reaction with the initial isoprene oxidation products which form SOA. Isoprene has been observed to decay after sundown, consistent with reaction by NO₃, and some typical lifetimes for this decay are 1.5-3 hours (Steinbacher 2005). Thus, one might expect a time delay on this order.

Page 8874 Line 18 Why was the maximum organic aerosol concentration used?

Response: The equilibrium partitioning calculation requires us to use a measured concentration of organic aerosol, not a dilution corrected one. Here we are attempting to compare the yield calculated from the modeled secondary oxidation product concentration and AMS data to the yield one would expect from the actual

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conditions in the chamber. The maximum OA concentration was used for the calculation because it occurred just after the rapid SOA growth period, before chamber dilution removed much of the SOA. This time is most directly comparable to the calculated yield. For a more clear comparison, we will calculate the yield from the second oxidation step by using the data at Hr 16:15 as well.

Page 8892 Fig 2. Provide example structures of NIT 1-4, here or in another table.

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

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