

Interactive comment on “Peroxy radical chemistry and OH radical production during the NO₃-initiated oxidation of isoprene” by A. J. Kwan et al.

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Response to Reviewers

We would like to thank the reviewers for their careful consideration of our manuscript, and welcome the opportunity to respond to their comments and integrate their suggestions into the revised manuscript.

Reviewer 1

1) p. 2263, line 13: The experimental conditions are clearly aimed at low NO_x conditions, and the authors make a broad claim here that these are also

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the relevant atmospheric conditions. However, there are atmospheric situations (urban environments), where higher NO_x levels at night are possible.

We will emphasize in the revised manuscript that our experimental conditions are representative of remote environments. Isoprene concentrations are generally higher in remote areas than urban areas, so low NO_x conditions are more relevant for our system, though as mentioned in this comment high NO_x conditions can be important in certain situations.

2) p. 2263, line 24: Is the thermal decomposition of N₂O₅ virtually immediate on the time scale of mixing? This should be quantitatively justified.

As we do when calculating isoprene nitrate yields with respect to reacted nitrogen, we can use NO₂ concentrations as a measure of N₂O₅ decomposition. After injection of isoprene, the NO₂ concentrations increase ~ 125 ppb within 5 minutes, which is also the approximate timescale of mixing in our chamber. Even if thermal decomposition of N₂O₅ were much slower than mixing, isoprene levels would still be higher than NO₃ levels by a factor of ~ 1000 (based on box model calculations described in our response to Reviewer #2's comment #14), so these conditions should still favor RO₂ + RO₂ reactions compared to RO₂ + NO₃ reactions. Prior to isoprene injection, the chamber is undisturbed for ~ 90 minutes to allow for N₂O₅ mixing, during which NO₂ increases linearly ~ 25 ppb, which is a much slower rate than after isoprene injection. Therefore, we attribute the rapid rise of NO₂ after isoprene injection to the reaction of NO₃ + isoprene.

3) p. 2267, line 21: The discussion of NO₂ levels in the system made me wonder if the authors specifically considered (and apparently discounted) possible RO₂ + NO₂ reactions in their model (I don't see a RO₂ + NO₂ reaction listed in Table 2).

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We have modified the model to include $\text{RO}_2 + \text{NO}_2$ reactions (as well as RO_2NO_2 decomposition) using estimated rate constants from Sander et al. ($k_{\text{RO}_2+\text{NO}_2} = 5\text{e-}11 \text{ molec}^{-1} \text{ s}^{-1}$; $k_{\text{RO}_2\text{NO}_2} = 20 \text{ s}^{-1}$). The addition of these reactions changes the final OH formation in each model run by $<1\text{ppb}$, so the basic conclusion that OH formation is most likely from $\text{RO}_2 + \text{HO}_2$ reactions still holds.

4) p. 2268, line 29: I'm not sure I understand how experimental conditions would affect the distribution of isomers. Is this expected to be sensitive to pressure and/or temperature, or some other experimental condition?

We write in that paragraph that the ratio of RO_2 isomers affects the final product yield because $\delta\text{-RO}_2$ radicals tend to lead to nitrates and $\beta\text{-RO}_2$ radicals tend to lead to non-nitrates. This ratio, however, would not be a fixed quantity if isomers interconvert, as suggested by Berndt and Böge (1997) and Peeters et al. (2009). The degree of interconversion is affected by the rate at which RO_2 become stable products relative to the interconversion rate, i.e., the magnitude of k_1 and k_2 with respect to $k_{\text{int}1}$ and $k_{\text{int}2}$ in Figure 1. Temperature and pressure may affect these rates, as well as the degree of mixing and the hydrocarbon and oxidant concentrations, which will affect the rates of $\text{RO}_2 + \text{RO}_2$, $\text{RO}_2 + \text{NO}_3$, etc. Because these conditions are different in the alternate studies of the isoprene + NO_3 reaction that we cite, this may explain the discrepancy in nitrate yields between studies. This will be clarified in the revised manuscript.

5) p. 2269, line 3: In the discussion of the carbon yield analysis, it is mentioned that some isoprene reacts immediately and that this complicates the analysis. Why couldn't a blank experiment be conducted (w/o N_2O_5) to determine the actual starting isoprene concentration in the chamber?

We performed such an experiment. That is why in the experimental section we

C3125

state "the amount of isoprene added corresponds to a mixing ratio in the chamber of $\sim 800 \text{ ppb}$ " (p. 2264, line 25). The reproducibility of this blank experiment is affected by factors such as tubing losses, variability in the volume of isoprene injected, and fluctuations in the chamber volume (the walls of the chamber are not rigid). The chamber volume is a function of factors such as temperature, pressure, and the number of instruments sampling. From experience, we estimate that such errors would lead to an uncertainty of $\sim 5\%$ (i.e., $\pm 40 \text{ ppb}$) in the concentration of isoprene during the actual experiment. Since we expect only $\sim 125 \text{ ppb}$ of isoprene to react, this 40 ppb uncertainty in isoprene would represent a large uncertainty for the determination of the carbon-based nitrate yield. Therefore, we use the CIMS measurements as a proxy for the amount of isoprene reacted, which corresponds well with the estimate based on the change in NO_2 levels.

6) p. 2269, line 19: Since OH production is a major finding of this work, I think it deserves some further elaboration. In particular, it would be helpful to include a figure with the relevant products (and associated m/z carriers) to accompany this discussion.

Such a figure will be included in the revised manuscript.

7) p. 2273, line 6: OH production has also been observed from aromatic systems (JPCA, 2011, 115, 5397-5407).

We will cite this and the companion work from this group (JPCA, 2010, 114, 10655) in the revised manuscript.

8) p. 2277, line 23: Exactly how is the mechanism analogous to the formation of bicyclic peroxy radicals for aromatic compounds?

Bicyclic peroxy radicals are formed in aromatic compounds when the peroxy

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group formed after the first oxidation step adds to one of the other double bonds in the aromatic ring. In our work, we propose that a similar addition can take place by RO_2 adding to one of the double bonds of an isoprene molecule, leading to low vapor pressure C_{10} compounds.

p. 2261, line 10 and many other places: I think the use of the term “dimer” is not appropriate. These compounds should be referred to as organic peroxides to emphasize that they originate from the self-reactions of peroxy radicals.

In the revised manuscript we will refer to these compounds as “ C_{10} organic peroxides” to emphasize both their origin and the fact that they are large compounds with low vapor pressures.

Table 1: please add a column that computes the percent yield of each of the products.

We will add this column to the table in the revised manuscript.

Reviewer 2

1) The production of OH seems to be central to discussion of results and implications in this manuscript but is not highlighted in the title or introduction. I suggest adding background on this question of additional oxidant sources upfront.

Based on the feedback of the preliminary reviews, we added mention of OH production in the title of the ACPD manuscript. We will also add some background of $\text{RO}_2 + \text{HO}_2$ reactions and OH production in the revised introduction.

C3127

2) (related to point 1) In the discussion of Figure 4 and in the figure itself: clearly you were tweaking the model to get more OH production. What determined the degree of your tweaks? Can you put any, even approximate, constraint on the likely amount of OH produced based on observed OH-isoprene products? If so it would be great to include the apparent branching ratio of OH production in the manuscript.

Due to the heterogeneous mixing in the chamber and the uncertainties in rate constants, the box model is not designed to quantitatively predict OH formation, but rather to evaluate the feasibility of competing hypotheses for OH production, specifically $\text{HO}_2 + \text{NO}_3$ reactions. While the rate constant of this reaction is well established, some of the other reactions that affect the concentration of HO_2 and NO_3 , such as $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{NO}_3$, are poorly constrained. Therefore, we sought to examine how sensitive OH production from $\text{HO}_2 + \text{NO}_3$ was to these constants and reduced them by factors of 10 and 100. This would magnify the $\text{HO}_2 + \text{NO}_3$ rate by reducing the magnitude of competing reactions of HO_2 and NO_3 . As shown in Figure 4, these changes favoring $\text{HO}_2 + \text{NO}_3$ do not increase OH production to levels seen in the experiment, which is why we do not believe that $\text{HO}_2 + \text{NO}_3$ is responsible for all the OH production in our experiment. This leads to our conclusion that $\text{RO}_2 + \text{HO}_2$ reactions are the major pathway to OH formation.

Although we believe that $\text{RO}_2 + \text{HO}_2$ reactions are the major pathway to OH formation in this experiment, other pathways such as $\text{HO}_2 + \text{NO}_3$ may contribute. In the manuscript we constrain the amount of OH produced based on the OH-isoprene products (9-20.5 ppb), but we do not attempt to calculate a branching ratio of OH production. In fact, we implicitly assume that all other pathways besides $\text{RO}_2 + \text{HO}_2$ are negligible. Due to the qualitative nature of the box model we do not feel it is appropriate to try to quantify this branching ratio. It would, however, be appropriate to explicitly state in the revised manuscript that our estimated OH yield from $\text{RO}_2 + \text{HO}_2$

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assumes that this is the exclusive pathway to OH. Therefore, our estimate should be considered an upper limit.

3) Table 1 and last paragraph of p. 2266: I'd like to be able to tell if this slow equilibration with surfaces in tubing/instrumentation is a big effect or not – is the peak mixing ratio likely a big underestimate of actual product yield or not? Can you provide any kind of uncertainty estimate due to this effect, e.g. based on other experiments with mass balance? In the heading in Table 1, I suggest labeling as “maximum/peak concentration” to remind/highlight this.

It is difficult to quantify the loss to surfaces because the loss processes depend on many parameters that are not known for these novel C₁₀ compounds, such as vapor pressure and affinity to the surfaces. Furthermore, these compounds have low concentrations which are smaller than the uncertainty in the mass balance determination (~ 25% from the CIMS calibration), so mass balance – which is a persistent challenge in atmospheric organic chemistry – would not be an appropriate technique for determining this uncertainty either.

To get an approximate idea of the losses, we can assume that condensation onto aerosol (SOA) is the most significant loss process for these compounds in the gas phase. We must further assume that all the SOA formed in the experiment (~ 10 µg/m³) consists exclusively of C₁₀ dinitrates (molecular weight ~ 300). With these assumptions, we calculate the equivalent of ~ 1 ppb of C₁₀ compounds in the aerosol phase, so our underestimation may be a factor of ~ 2, but this is highly uncertain due to the necessary simplifications.

4) Please indicate if the yields are determined on a molar or mass basis.

The yields are on a molar basis, which will be made explicit in the revised manuscript.

C3129

5) Last paragraph on p. 2268: why would the possibility of radical inter-conversion make the distribution of isomers more sensitive to initial conditions?

We address this question in our response to comment 4 from Reviewer 1.

6) Last paragraph of section 3.1, p. 2269: here you say nitrate yields should be considered upper limits, while in the abstract you list yield as “> ~80%”, should this be “< 80%”?

The “>” sign appeared in the abstract originally because calculating the nitrate yield with respect to reacted nitrogen yielded a range of 80-90%. To avoid confusion in the revised manuscript, we will remove the “>” sign so that the nitrate yield is stated as “~ 80%.”

7) Section 3.2: box model is introduced early – do you really need it to demonstrate that HO₂+NO cannot possibly be important? Seems you can say this without the model, but it really is needed for the later RO₂+HO₂ branching – I would move its discussion down there.

Given the low levels of NO detected in the chamber, it may not have been necessary to use the model to demonstrate that HO₂ + NO reaction is unimportant. But the reactions do not take place in a well-mixed system, so the NO concentrations where the reaction is taking place may be higher than the measurements. Also, NO is formed as a minor channel of NO₂ + NO₃ reaction, and if that NO reacts rapidly with HO₂ to form OH, it may not be detected by the NO detector. So we use the model to give greater support to an intuitive conclusion.

8) last paragraph on p. 2272: RO₂ /HO₂ reactions from isomerized nitrooxy RO₂

C3130

are ignored, but earlier you pointed out that this isomerization was facile – how to reconcile this?

For the revised manuscript we will include the isomerized RO₂, and add the CIMS signal at m/z 264 (isomerized ROOH) to the denominator in the calculation at the top of page 2273. Since the isomerized RO₂ is a minor component of the total RO₂ (Table 1), this change does not alter our estimate significantly; the new range is 38%-58% compared to 42%-62%. It will be emphasized that this is an estimate for the isomeric mix of RO₂ in our experiment, as the available data do not allow us to determine this yield for each individual isomer, e.g., from (1,4) additions, (4,1) additions, and RO₂ undergoing 1,5-H shifts. Nonetheless, the RO₂ from (1,4) addition is probably the most abundant isomer, so the OH yield from this isomer is likely close to the experimentally determined range.

9) Last sentence above section 3.2.1 p. 2273: Elaborate please – why do you expect resonance stabilization of the radical reactant to preference the radical propagation product channel?

The radical propagating channel (RO₂ + HO₂ → RO + OH) is more favored (thermodynamically) when the products have lower enthalpies with respect to the reactants. Thus, this channel is favored for RO with lower enthalpies, such as RO with resonance stabilization. We will add this explanation in the revised manuscript.

10) last paragraph, p. 2275: “There remain many uncertainties regarding the mechanism of RO₂ + RO₂ reactions (Dibble, 2008), so it is difficult to assess whether reported ROOR formation (or lack thereof) is a result of the particular radicals studied or the analytical techniques employed to study their reaction.” Sounds like you’re pointing out discrepancies in previous measurements of RO₂/RO₂ to yours for isoprene? I don’t see a huge discrepancy as

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you’ve set it up – perhaps you can start this paragraph in away that highlights the difference you’re trying to point out? Is it the difference between 38% and 50%?

This sentence refers to the fact that we measure appreciable amounts of ROOR compounds in this experiment, although “channel (R9) [the ROOR forming channel] is generally considered negligible” (p. 2275, line 9). This discrepancy between our observations and the prevailing theory is the difference we are pointing out.

11) Top of 2277: Why would O₂ abstraction be faster for these radicals? Is there a structural explanation?

We do not have a physical explanation for why O₂ abstraction would be faster, nor is it our intention to state that it is faster. We merely mention that faster O₂ abstraction is a possible explanation for why we see a higher HO₂ yield than in other systems. More study would be necessary to determine if that is true.

12) At end of section 3.5: add a wrap-up statement to make clear what you’re saying: you’re proposing that RO₂ + isoprene might be an important reaction pathway here

We discuss the possible importance of RO₂ + isoprene in the implications section, but can also add an additional statement here for further clarity.

13) Top paragraph on p. 2280: RO₂-RO₂ reactions are sped up by NO₃ electron- withdrawing group: what about your resonance-stabilized radical

The suite of RO₂ + RO₂ (and RO₂ + HO₂) reactions for which detailed kinetic and/or product studies have been performed is limited, and to our knowledge no

C3132

studies on the influence of resonance stabilization (such as with aromatic RO₂) have been performed. The role of resonance stabilization is an important question, to which we allude in our concluding remarks: “more studies focused on nitrooxy and allylic peroxy radicals, as well as larger peroxy radicals, are warranted.” We will explicitly mention the possible influence of resonance stabilization in the revised manuscript in the paragraph in question.

14) Since you emphasize a few times the sensitivity to initial conditions, maybe a comment is warranted on how much greater than ambient conditions this experiment is. Do you expect the sensitivity to be primarily in the RATIO of NO₃ to isoprene?

As discussed in Ng et al. (2008) and the last paragraph of the introduction, the ratio of RO₂ + RO₂ reactions to RO₂ + NO₃ reactions is one of the key parameters affecting the product yield. In our experiment, this is determined by the [isoprene]:[NO₃] ratio.

High [isoprene]:[NO₃] ratios can exist during the hours right before sunset, because although emissions of isoprene are low, so too are the concentrations of OH and NO₃. It is difficult to quantify a typical ratio for this situation, however, because of the wide range of [isoprene] and [NO₃] in the ambient atmosphere. Also, in many cases [NO₃] is near 0 at sunset, and as NO₃ is formed isoprene concentrations drop rapidly, so the ratio will also change rapidly. Likewise, it is also difficult to assign an [isoprene]:[NO₃] ratio in our experiment because the reaction does not occur under well-mixed conditions.

Although we cannot give exact ratios, rough estimates of our experimental [isoprene]:[NO₃] ratio give environmentally feasible results. To estimate the [isoprene]:[NO₃] ratio in our experiment, we run our box model (using the base

C3133

conditions described in table 2) with [isoprene] = 1 ppm and [N₂O₅] = 150 ppb, which yields a peak [NO₃] of ~ 1 ppb, or an [isoprene]:[NO₃] ratio of ~ 1000. Apel et al. (J. Geophys. Res., 2002) and Brown et al. (2009) find [isoprene] ~ 1 ppb at sunset in Northern Michigan and New England, respectively, so [NO₃] levels of ~ 1 ppt would yield similar [isoprene]:[NO₃] ratios. Furthermore, studies of daytime isoprene + NO₃ reactions find [isoprene] ~ 10 ppb and [NO₃] ~ .5 ppt, or an [isoprene]:[NO₃] ratio of ~ 20,000 [Brown et al. (2005); Fuentes et al. (2007)]; RO₂ + RO₂ would also likely be more favored with respect to RO₂ + NO₃ in these cases. In the ambient atmosphere, however, HO₂ and NO will also influence the final product yield and must also be considered.

While the [isoprene]:[NO₃] ratio in our experiment may be representative of the ambient atmosphere, their individual concentrations are much higher than typical. This favors the formation of secondary organic aerosol, so it is possible that we underestimate the gas-phase yield of low vapor pressure C₁₀ compounds. The ambient atmosphere, though, has pre-existing particles allowing for condensation of low vapor pressure compounds, so this underestimation may be negligible.

Technical corrections: a) Caption to Fig. 1 : suggest “are detected by the CIMS instrument as CF₃O- adducts at the indicated. . .” b) Caption to Table 2: suggest “for box model assessment”

These changes will be made in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2259, 2012.

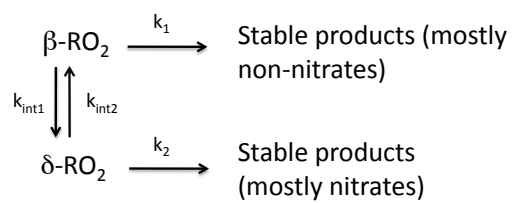


Fig. 1. Schematic of RO₂ isomer interconversion