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Interactive comment on “Hydroxy nitrate production in the OH-initiated oxidation of alkenes” by A. P. Teng et al.

Anonymous Referee #2

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The paper by Teng et al reports on reaction chamber experiments leading to determination of the branching ratios for production of organic nitrates from a series of alkenes, from C2 to C8, along with estimates of the distribution of isomers from OH and O₂ addition to the two carbon atoms. This is a well-done piece of work, resulting in a self-consistent set of branching ratios, and a study that was sorely needed, given the paucity of data on this subject, and the importance of alkenes to atmospheric chemistry, in general. I found the approach to be clever, with a good combination of analytical approaches to tackle the problem. A basic result is that when the branching ratios are plotted vs the number of "heavy atoms", i.e. including the -OH as such, the results of this study are consistent with those from Arey et al. for simple alkyl radicals. This is an important set of data, and the paper is well-written and the study well-executed.

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It thus should be published, once a significant issue is dealt with. That issue is that, since this result is so important, the quantitative results should be solid, and defensible. In terms of analysis of the results it is. However, the bottom line for confidence in the result is the calibration of the CIMS used for quantitation, for which there is very little discussion, and the method is actually assumed to be without uncertainty. It is stated on page 6728, line 12, that the GC-TD-LIF enables "absolute calibration of the CIMS sensitivity to the individual alkyl nitrates". But this is not an absolute calibration in any sense of the term. An absolute calibration would involve gas phase standards of the pure compounds with known concentrations determined in some reliable way, e.g. involving gravimetric preparation. For the method used to rise to the level of a good secondary standard calibration, it would have to be known that indeed the TD yields of NO₂ are 100%, in the N₂ carrier gas, and at the concentrations of the organic nitrates in the peaks as they elute. One can easily imagine circumstances for which the yields might be <100% in N₂, even if they are known to be 100% in air. In the presence of O₂, the RO radical produced will react with O₂ and be destroyed. However, in N₂ this doesn't happen, so that RO + NO₂ recombination could more easily occur, e.g. once the gas cools down after the oven. Interestingly, if this were the case, it would lead to RONO₂ concentrations in the peaks that were underestimated by the TD-LIF, leading to a CIMS sensitivity that is too large. Thus in this case, the CIMS-determined RONO₂ yields would be underestimated. In any case, it remains to be demonstrated that the TD yields are 100%, and the same for all organic nitrates, at the relevant concentrations in N₂. The authors cite Lee et al., but that paper similarly does not report NO₂ yields for hydroxy nitrates, or any other nitrates, in the GC carrier gas. I note that the results from this paper would also be much more convincing if the total RONO₂ from the TD-LIF were determined from direct sampling of the chamber, since this is quite simple, according to existing literature, and then that total could be compared with the CIMS total, based on the GC-TD-LIF calibration. If they agreed, then there would be considerably more confidence in the results. If I understand correctly and this was not done, that seems odd. Or was it in fact done as described in Section 3.3? Or are

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the absolute yields done by GC-TD-LIF, as indicated on page 6734, line 14? The experimental details for the TD-LIF part of the absolute yield experiments are a bit hard to follow. If the absolute yields were done by GC-TD-LIF, then you need gas phase standards for some hydroxy nitrate, to get an absolute yield, or you have to account for column losses. But you can't just state that the yield is 100% in this case, without clearly presented experimental evidence. Since the TD-LIF is the basis of all quantitation in this paper, relative sensitivity data for some representative species is certainly warranted. On page 6732, lines 14 and 27, and on page 6733, line 24, the issue of the NO₂ yield is not even mentioned as one of the possible uncertainties. Until proof is shown that the NO₂ yield is indeed 100%, then one could argue that this is the largest source of uncertainty. This issue could be resolved by either calibration of the CIMS independently for one or more of the pure compounds, and comparison of calibration factors, or through proof that the NO₂ yield is 100% for all compounds in the carrier gas. Hopefully, this is readily achievable, or known, but not stated explicitly in the paper. I note that the analytical section on the calibration in Section 2.3 is a bit confusing, or not immediately apparent, in that the GC analysis is for a discrete sample in the form of a Gaussian peak, with a concentration in N2 that is continuously changing over the width of the peak; can you explain a bit more clearly how you convert the hopefully known integrated amount of RONO₂ in that peak into a CIMS sensitivity in some units like Hz/ppt? More minor issues are listed below in the order they arose in the manuscript.

1. I think the word "scatter" on page 6724, line 17 is not quite right. Within each of the existing literature data sets, the yields are not particularly scattered. Rather, for a particular peroxy radical (and you have to include this paper to even say this), the literature data cover a rather wide, conflicting range.
2. Page 6726, lines 306: what was the NO_x concentration for the hydroperoxide yield measurements? Was it measured? Is it important that there are not multiple reaction paths available to the peroxy radicals? Lines 21-22 - it is not clear why the amount of

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air in the chamber impacts conversion of NO to NO₂ (in a positive way).

3. Page 6730 line 5, remove the word "of". Line 7 - define a and b. The sentence at the bottom of this page needs to be split into two sentences.
4. Page 6731, line 11, you should move the (Y=...) to after the word "yield", since this is the yield, not the ratio. Line 22 - the loss was estimated iteratively, correct?
5. Page 6732, line 10 should say rate "constant", and the word "the" should precede "same". Line 18 - does the word "the" come after propene?
6. Page 6734, line 4 - by "scale" you mean linear fit?
7. Page 6735, line 26, you need a - after the "methyl".
8. Page 6736, line 4 - explain how the transmission was measured.
9. Table 5 - can you provide uncertainties for the -OOH % isomer distribution? I note that the data in this Table represent highly valuable information, and they will become widely utilized once published, so the uncertainties are important.

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