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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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General comments

This manuscript describes environmental chamber experiments aimed at determining the hydroxynitrate branching ratios for the reactions of alkene-derived hydroxyl peroxy radicals with NO. The simultaneous use of GC, CIMS, and TD-LIF techniques allows for the novel determination of isomer-specific branching ratios (due to the GC approach) without the need for the preparation of authentic hydroxynitrate standards (due to the TD-LIF approach). The main finding of the work is that the branching ratios are larger than some previous measurements for alkene-derived hydroxynitrates, but in good agreement with previous measurements for alkane-derived nitrates. Thus, the authors are able to propose a quite simple model for predicting nitrate yields that is only dependent on the number of non-peroxy moiety heavy atoms in the peroxy radical re-

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actant. This finding is also important in that it suggests that nitrates are more efficiently formed than previously thought, with a correspondingly important effect on air quality (as demonstrated in the manuscript by an analysis of field observations in the Houston area). The work has been carefully planned and executed, and the manuscript is clearly written. For these reasons, this study is quite appropriate for Atmospheric Chemistry and Physics.

Specific comments

Experimental method: I am somewhat confused by how the actual experiments were carried out. From the text, I gathered that the alkenes were studied one at a time (because of the absolute concentration measurement methods used, relative methods are not necessarily needed). However, Table 1 indicates that two or three organic compounds were added in each experiment. While I can infer that ISOPN was added as an internal standard for some experiments (1-7), I don't understand why it wasn't used in all experiments. Also, for experiments 8-12 and 14-21, several alkenes were added, presumably to allow for "direct" relative measurements. The authors should more fully explain the rationale and the details of the experimental method in a revised version of manuscript. In particular, the use of the word "relative" needs to be carefully used, as I suspect that were some experiments in which relative quantities were directly determined, while there are other relative quantities that were calculated from separate experiments.

p. 6730, line 5, typo: delete "of" that occurs before "beta"

p. 6730, line 9: The word "simple" is not very descriptive. It would be more clear to state that the CF3O- CIMS technique is sensitive only to hydroxy-functionalized products, which are not formed in OH abstraction initiated oxidation mechanisms.

Figures 2 and 7: In a similar vein to the comments above about the experimental methods, it is not clear whether the data given in these figures is for a single experiment in which many alkenes are present (I don't think so, as Table 1 doesn't indicate any

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experiment with these conditions). It would be helpful for the authors to indicate which experiments from Table 1 were used to generate the data plotted in Figures 2 and 7.

Figure 3: It would be helpful if the authors annotated this figure with proposed isomeric structures for each of peaks in the chromatogram.

p. 6736, line 5: The derived linear model for hydroxynitate branching ratios is inappropriate for ethene (this data point is left out of the analysis portrayed in Figure 4; if one calculates the hydroxynitrate branching ratio for ethene, the model predicts an unphysical negative branching ratio). This should be explicitly pointed out.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 6721, 2014.