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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 #3

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General Comments:

In this manuscript the authors describe results of laboratory experiments in which they investigated the formation yields of beta-hydroxynitrates from the reactions of a series of 1-alkenes with OH radicals in the presence of NOx. The experiments were conducted in a small Teflon reaction chamber and yields were measured using a combination of chemical ionization mass spectrometry, thermal decomposition of nitrates with NO2 analysis, and gas chromatography. The experiments and data analysis appear to have been very carefully and thoroughly conducted. All aspects of the study are described in great detail. The results are interesting and important since they indicate that the yields of beta-hydroxynitrates are twice as large as those reported in a number of previous studies and are similar to yields of alkyl nitrates that have been measured for reactions of alkanes of the same carbon number. These higher yields can have a significant effect on model predictions of the sequestering of NOx and O3 formation.

The paper is certainly appropriate for ACP and I recommend it be published. My major suggestion (as discussed more specifically below) is that the authors provide a more careful and complete discussion of previous work rather than hoping that future readers will gather this information on their own by reading the referenced papers. Considering the large discrepancy between the results reported here and most previous measurements, and the fact that it is not yet obvious (at least to me) which results, if either, are correct, the authors could do a service to readers by providing a more careful discussion of the work that conflicts with their results instead of emphasizing points of agreement. This seems especially appropriate since the most comprehensive previous studies are those that disagree.

Specific Comments:

1. Page 6724, lines 9–25 and Page 6734, lines 22–24: I'm not sure the authors are justified in using literature measurements of total organic nitrate yields to support the conclusions of this paper when those measurements are not quantitative and they are known to overestimate the yields of beta-hydroxynitrates. It has been noted by Roger Atkinson in a personal communication that their FTIR data (Atkinson et al. 1985 and Tuazon et al. 1998) provided only semi-quantitative estimates of beta-hydroxynitrate yields, because in addition to the beta-hydroxynitrates formed from the initial RO2 + NO reaction the products included organic nitrates formed from other RO2 radicals, and in experiments that were conducted with high NO2 concentrations they included organic nitrates formed from reactions of alkoxy radicals with NO2. Here it is claimed that the contributions from these other sources should be small, but no evidence is provided as to why.

2. Page 6724, lines 9–25 and Page 6734, lines 24–26: I wonder about the comparison with the results of the CIMS study by Patchen et al. (2007). Although the results of

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the present study agree with the beta-hydroxynitrate yields measured by Patchen et al. (2007) for 1-butene and 2-butene, it is my understanding that the authors have recently measured the yields of beta-hydroxynitrates formed from isoprene using the same techniques they employed here, and that those values were twice as high as those reported by Patchen et al. (2007) for isoprene. If so, this discrepancy should be noted, and might this not lead to some concerns about the CIMS measurements?

3. Page 6724, lines 9-25, and Page 6735, lines 3–4: The authors seem to be implying that O'Brien et al. (1998) underestimated the yields of beta-hydroxynitrates because of losses in their GC column. Why might GC analysis work fine in the present study but not for O'Brien et al.? Was something done here to avoid the problems the authors think O'Brien et al. encountered in their GC analysis? It seems to me worth noting that O'Brien et al. calibrated their entire system, from sampling through detection, using authentic standards sampled from a chamber, and that this should have accounted for the artifacts that are suggested here.

4. Page 6724, lines 22–25: In a number of places in the manuscript the authors emphasize the importance of direct sampling, but they do not seem to be aware that the measurements made by O'Brien et al. (1998) were made using direct sampling from their chamber into their GC.

5. Table 5. It might be noted that the isomer ratios agree quite well with those measured/ predicted by the results of Matsunaga and Ziemann, PNAS (2010).

6. There are a few studies published by Ziemann and co-workers that are not discussed in any detail in this paper, but which yielded results that are consistent with those of O'Brien et al. (1998). Unlike O'Brien et al. (1998) and the present study, however, they used HPLC-UV analysis of filter extracts to quantify beta-hydroxynitrates in particles under conditions when these compounds were present entirely in the particle phase (Matsunaga and Ziemann, JPCA, 2009). For reactions of ∼C14–C17 internal alkenes and 1-alkenes they obtained yields (relative to OH addition) that were ∼1/2 the alkyl

nitrate yields they recently measured for reactions of n-alkanes of the same carbon number by GCFID analysis (Yeh and Ziemann, JPCA, 2014). In both studies the yields reached a plateau at ∼C15, consistent with the model predictions of Arey et al., JPCA (2001). Furthermore, when the model of Arey et al. (2001) was used to extrapolate the plateau yields for 1-alkenes to smaller carbon numbers the results agreed well with the values measured by O'Brien et al. (1998). Although the studies employed filter sampling rather than direct sampling, the experimental methods are quite simple and it was straightforward to (1) correct for minor losses by secondary OH reactions, (2) correct for relatively small particle wall losses during sampling, (3) verify that the beta-hydroxynitrates are stable, (4) verify that filter extraction was quantitative, and (5) quantify beta-hydroxynitrates by HPLC-UV using authentic calibration standards prepared by gravimetric methods.

7. Do the authors have any recommendations for improving future measurements on these systems, either using their approach or others?

Technical Comments:

None.

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