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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.

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We thank the reviewer for these comments.

''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."

We have expanded the discussion of how this work compares with previous work in the revised manuscript. This is contained in the results section.

''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-hydroxy nitrates. 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-hydroxy nitrate yields, because in addition to the beta-hydroxy nitrates 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."

Thank you for this comment – we agree. Given that methyl nitrate (formed from methoxy radical + $NO_2$) is a potentially large contribution to the organic nitrate measured in both the Atkinson et al., 1985 and Tuazon et al., 1998 papers, these studies provide only upper limits to the beta-hydroxy nitrate yields. The discussion in the paper has been revised.

''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 the present study agree with the beta-hydroxy nitrate 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-hydroxy nitrates 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?"

We note that Patchen et al. (2007) had synthesized standards for HN from 1-butene and 2-butene to calibrate their branching ratio measurement. Without authentic standards for isoprene hydroxy nitrates, they selected the hydroxy nitrate sensitivity derived from 2-butene to calibrate the isoprene hydroxy nitrates. Recent evidence from the Caltech FIX-CIT campaign (Nguyen et al., 2014) has indicated proton ion transfer chemistry may induce significant fragmentation for isoprene hydroxy nitrates though the extent of this is likely dependent on the conditions of the ion chemistry. This may explain some of the difference between the Patchen et al study and our recent, but yet unpublished yields for isoprene hydroxy nitrates. We therefore believe the discussion of isoprene hydroxy nitrates falls outside the scope of the paper.

"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-hydroxy nitrates 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."

We have spent more time to try to understand why our results differ from O'Brien et al., 1998. A key difference between O'Brien et al., 1998 and the present study are the concentrations of reagents used in the chamber study. Modeling the experimental conditions described in the O'Brien et al., 1998 leads us to believe that significant conversion of $\mathrm{NO}$ to$\mathrm{NO_2}$ occurred before UV lights were turned on for those experiments which have initial $\mathrm{NO_x}$ concentrations greater than 100ppmv. This is important as the resulting high concentrations of $\mathrm{NO_2}$ would produce a significant amount of atomic oxygen upon UV light exposure. We estimate substantial alkene loss (< 50%) in O'Brien et al. was by $\mathrm{O(^3P)}$ chemistry. This would lead to significant underestimation of the branching ratios to form hydroxy nitrates for many of the alkenes. The details of this analysis are provided as a supplement.

This discussion has been added to the manuscript.

"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."

The manuscript now more carefully explains what we mean by the term 'direct sampling'. In short, we mean without chromatographic separation, direct sampling from the experiment bag through a 1.5m $\frac{1}{4}$" Teflon tube (residence time of <0.2 s). This mode has substantially fewer surface interactions than the GC mode of sampling.

"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)."

We have now cited this study in Table 5.

"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-hydroxy nitrates 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-hydroxy nitrates are stable, (4) verify that filter extraction was quantitative, and (5) quantify beta-hydroxy nitrates by HPLC-UV using authentic calibration standards prepared by gravimetric methods."

Recent work (Zhang et al., PNAS, 2014) has shown secondary organic aerosol mass can be substantially underestimated due to vapor wall loss, with underestimation ranging from 1.1 for saturated C12 alkanes up to a factor of 4 for toluene under high NOx conditions and in a chamber in which seed to wall surface area ratios are quoted to be less than $1 \times 10^{-3}$. Zhang et al., 2014 has found that the SOA yield is highly dependent on 1) the rate of oxidation and the duration of the experiment, 2) the precursor VOC concentration, 3) the chemical pathway, and 4), the seed surface area relative to the chamber surface area.

For the conditions described in Matsunga and Ziemann (2009) as compared to Yeh and Ziemann (2014) it is not clear whether wall loss is a significant factor in Matsung and Ziemann (2009). Matsunga and Ziemann (2009) had OH concentrations of approximately $3 \times 10^7$ molec cm$^{-3}$, and a seed to wall surface area ratio of $8.2 \times 10^{-4}$ (assuming 400 ug m$^{-3}$ of particles at 100nm diameter with a density of 1.1 g cm$^{-3}$ and a spherical chamber with volume 5900L). Yeh and Ziemann, ACS, 2014 recorded negligible organic mass on the particles after oxidation of n-alkanes at 100ug m$^{-3}$ particle concentration for 100nm particles in a chamber with 8200L volume, equating to a total particle to chamber surface area ratio of $2.3 \times 10^{-4}$ (assuming a spherical chamber and 1.1g cm$^{-3}$). In this study, Yeh and Ziemann (2014) found that above C12, 20-85

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

For GC analyses, especially those involving labile compounds, it is beneficial to assess the analyte transmission through the gas chromatograph. We suspect that humidity, metal surfaces, elevated temperature, elevated pressures, acidity/basicity, and high concentrations may cause losses in the GC setup described in this paper. We found

it particularly useful to continue reducing the length of the GC columns until stable transmission (and isomer distribution) were achieved between column lengths.

We also recommend experiments be conducted with $NO_x$ levels at sufficiently low levels (< 100ppmv) to avoid significant production of $O(^3P)$ to avoid the complication of significant quantities of other oxidants.

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C12517/2015/acpd-14-C12517-2015-supplement.pdf

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