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Comment

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

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We have conducted additional experiments to measure the absolute hydroxy nitrate branching ratios of propene, 1-butene, and 1-hexene. We have also measured absolute hydroxy nitrate branching ratios for 2-methyl 1-butene and 1-pentene. For propene, we have found that the yield reported in our initial submission (5.3%) was biased high due to an error in the quantification of propene. The corrected yield is $4.1 \pm 2\%$. In some of the additional experiments, 1,2 butanediol was added along with propene to serve as a relative decay partner, which allowed us to infer the alkene decay independent of the GC-FID. Replicate experiments to determine nitrate yield for 1-butene and 1-hexene were well within error of the original estimates. We have also corrected an error in our

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data analysis for the C₂ and C₄ derived hydroxy nitrates, increasing their relative yields by 20% and 30%, respectively.

The analysis for determination of the absolute branching ratios has been improved. We now calculate an overall branching ratio for individual compounds by averaging multiple experimental results, and applying a reproducibility uncertainty (20

The overall impact of our modified analysis is a modest change in the slope and intercept of the dependence of branching ratio to form hydroxy nitrates on the number of heavy atoms. The revised results do not alter the conclusion that the beta hydroxy nitrate branching ratios are, within error, equivalent to the alkane branching ratios.

We have also conducted a number of additional experiments to determine hydroxy hydroperoxide isomer distributions. The details of these experiments are explained in Author Comment 2. In brief, we have found that our initial results were likely impacted by RO₂ + RO₂ chemistry, resulting in biased ratios of hydroxy hydroperoxides isomers. The revised results indicate that for most alkenes studied, the hydroxy hydroperoxides isomer distribution is different than that of the hydroxy nitrate isomer distribution. Assuming unity yield of hydroperoxides and similar CIMS sensitivities between isomers, our revised results indicate that α_n increases with increasing peroxy radical substitution for beta hydroxy peroxy radicals. For primary and secondary radicals, this finding is in agreement with Cassanelli et al. (2007), and more broadly the work of Arey et al. (2001, and references therein). For tertiary nitrates, our results disagree with the previous literature which has either shown tertiary peroxy radicals to have either lower or similar branching ratios than secondary peroxy radicals (Orlando and Tyndall, 2012 and references therein). The difference between our results and that of Cassanelli et al. (2007) is consistent with significant losses of tertiary nitrates in the Cassanelli et al. (2007) study as has been previously suggested by Orlando and Tyndall (2012).

We have conducted one additional experiment to evaluate our assumption of unity yield of hydroxy hydroperoxides for methylpropene. We used both the GC-FID and our triple

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quadrupole operated in positive mode to quantify the production rate of acetone in the oxidation of methylpropene in an HO₂ dominated environment. Acetone is expected to be a major non-hydroperoxide product of the HO₂ + RO₂ radical recycling channel. Both methods are sensitive to acetone (detection limit sub-ppb level). However, the GC-FID acetone measurement has significant interference from the hydroxy hydroperoxides. The results indicate that the yield of acetone is less than 5%.

References

Cassanelli, P., Fox, D. J., and Cox, R. A.: Temperature dependence of pentyl nitrate formation from the reaction of pentyl peroxy radicals with NO. *Phys. Chem. Chem. Phys.*, 9(31), 4332-4337, 2007.

Orlando, J.J. and Tyndall, G.S.: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, *Chem. Soc. Rev.*, 41, 6294–6317, 2012.

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