

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.

“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).”

Many of the absolute yield experiments were conducted with multiple alkenes in a single experiment for convenience. Because the aldehyde products do not interfere in the determination of the alkenes using GC-FID, yield measurements can be done with multiple alkenes oxidized in the same experiment. The reviewer is correct in stating

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relative methods are not needed to report branching ratios and this has been corrected in the experimental details section.

“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.”

ISOPN was added in some cases to measure the rate of ISOPN decay relative to propene and not as an internal standard to measure hydroxy nitrates. These experiments were reported by Lee et al., 2014. This has been clarified in the revised manuscript.

“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”

We apologize for the lack of detailed explanation. The updated manuscript more clearly differentiates absolute yield experiments from relative yield experiments and more fully explains the details of the experiments. The major difference between relative and absolute yield experiments pertains to the amount of alkene oxidized. Relative yield experiments limit oxidation of the parent HC to <10% in all cases to reduce uncertainties associated with temperature variation and with loss of hydroxy nitrate via OH and wall loss. The analysis of the relative yield experiments also reduces uncertainty through cancellation of correlated errors associated with determination of total chamber volume and the use of the GC-FID. The relative yield determination relies mainly on the ratio of OH rate constants, the ratio of initial alkene concentrations, the ratio of HN sensitivities, and the ratio of HN signals. In each relative yield determination, only the ratio of OH rate constants and ratio of HN sensitivities are determined outside the

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given experiment. The relative yield experiments provide us with higher precision data to directly compare the effect of structure on nitrate branching ratios. As shown in the paper, the relative branching ratios show a strong linear dependence on the number of heavy atoms (not including the oxygens in the peroxy radical), N . To place these relative branching ratios on an absolute basis, the best fit of all the independently determined absolute branching ratios as a function of N is used. More specifically, this was accomplished by scaling the relative branching ratio data by the ratio of the absolute fit slope to relative fit slope and re-fitting. This method places the relative data on an absolute basis with lower uncertainty than using a single absolute yield of one compound.

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

Corrected

"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."

The word "simple" has been replaced with "CIMS instrument is insensitive to singly functionalized carbonyl or nitrate compounds formed from the OH H-abstraction channels."

"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 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 2 and 7 show data only from Experiment 19. This is now noted in the caption of both figures.

"Figure 3: It would be helpful if the authors annotated this figure with proposed isomeric

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structures for each of peaks in the chromatogram."

Structures added.

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

Ethene HN branching ratio from HOCH₂CH₂OO radical contains 3 heavy atoms (excluding the peroxy oxygen atoms). Using the relationship in the discussion manuscript, one calculates $\alpha = 1.6\%$. Using the relationship recommended in the revised manuscript, one calculates $\alpha = 2.5\%$.

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

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