Atmos. Chem. Phys. Discuss., 14, C12524–C12526, 2015
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Atmospheric Chemistry and Physics Discussions

ACPD

14, C12524–C12526, 2015

Interactive Comment

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

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 ± 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 C_2 and C_4 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 $RO_2 + RO_2$ 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 HO_2 dominated environment. Acetone is expected to be a major non-hydroperoxide product of the $HO_2 + RO_2$ 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%.

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

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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 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 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 structures for each of peaks in the chromatogram."

Structures added.

''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 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 $HOCH_2CH_2OO$ radical contains 3 heavy atoms (excluding the peroxy oxygen atoms). Using the relationship in the discussion manuscript, one calculates α = 1.6%. Using the relationship recommended in the revised manuscript, one calculates α = 2.5%.

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

Atmos. Chem. Phys. Discuss., 14, C12504–C12512, 2015
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We thank the reviewer for these comments.

‘’It is stated on page 6728, line 12, that the GC-TD-LIF enables "absolute calibration of the CIMS sensitivity to the individual alkyl nitrates". But this is not an absolute calibration in any sense of the term.”

We agree with the reviewer comment and the text has been reworded to read: “The concurrent elution of alkyl nitrates was monitored in parallel by both the CIMS and TD-LIF instruments, enabling secondary calibration of the CIMS instrument by the TD-LIF for the individual hydroxy nitrates.”

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‘’An absolute calibration would involve gas phase standards of the pure compounds with known concentrations determined in some reliable way, e.g. involving gravimetric preparation. For the method used to rise to the level of a good secondary standard calibration, it would have to be known that indeed the TD yields of NO2 are 100%, in the N2 carrier gas, and at the concentrations of the organic nitrates in the peaks as they elute. One can easily imagine circumstances for which the yields might be < 100% in N2, even if they are known to be 100% in air. In the presence of O2, the RO radical produced will react with O2 and be destroyed. However, in N2 this doesn’t happen, so that RO + NO2 recombination could more easily occur, e.g. once the gas cools down after the oven.”

We apologize for the lack of detail concerning the operation of the TD-LIF. Oxygen was added to the carrier gas just prior to entrance into the oven which converts RONO2 to RO + NO2. The oxygen concentration is added at a mixing ratio that converts 100% of a known (gravimentric) isopropyl nitrate concentration in the experiment bag as shown in the figure below. This figure has been added into the Supplement of the revised manuscript. Direct TD-LIF sampling was compared to a GC sampling. These tests showed no losses for isopropyl nitrate in the GC lines. A more detailed description of the TD-LIF instrument and the tests conducted to evaluate its performance have been added to the revised manuscript.

‘’Interestingly, if this were the case, it would lead to RONO2 concentrations in the peaks that were underestimated by the TD-LIF, leading to a CIMS sensitivity that is too large. Thus in this case, the CIMS-determined RONO2 yields would be underestimated. In any case, it remains to be demonstrated that the TD yields are 100%, and the same for all organic nitrates, at the relevant concentrations in N2.”

Due to the difficulty of quantitative gravimetric additions of isoprene hydroxy nitrates to the gas phase and lack of other hydroxy nitrate standards, it was not possible to conclusively determine the hydroxy nitrate conversion efficiency to NO2 in the TD-LIF at the relevant concentrations, as the referee notes. In the paper, yields are calculated

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under the assumption that the NO_2 yield from these nitrates is 100

‘’I note that the results from this paper would also be much more convincing if the total RONO2 from the TD-LIF were determined from direct sampling of the chamber, since this is quite simple, according to existing literature, and then that total could be compared with the CIMS total, based on the GC-TD-LIF calibration. If they agreed, then there would be considerably more confidence in the results. If I understand correctly and this was not done, that seems odd.‘’

The isoprene hydroxy nitrate (ISOPN) concentrations were measured directly by TD-LIF after addition of only ISOPN into the chamber. This measurement was, however, problematic due to long equilibration times (< 3 hours) resulting from low sampling flow and small diameter tubing in the TD-LIF instrument optimized for GC use. The sensitivity as determined by this measurement was 10-30% greater than the sensitivity determined through the GC for ISOPN compounds.

Direct sampling of the alkene-derived hydroxy nitrates discussed in this paper was not possible because authentic standards for these species were not available, and post-oxidation chamber air contains copious levels of NO2. We have also found that high concentrations of hydrogen peroxide disturb the measurements of nitrates and NO2 in the TD-LIF, particularly in the presence of NO. Using gas chromatography allows measurement of hydroxy nitrate yields without these interferences.

These details have been added to the manuscript.

‘’The experimental details for the TD-LIF part of the absolute yield experiments are a bit hard to follow. ‘’

The experimental setup and discussion has been revised to more clearly describe how the measurements were made.

‘’If the absolute yields were done by GC-TD-LIF, then you need gas phase standards for some hydroxy nitrate, to get an absolute yield, or you have to account for column losses. But you can't just state that the yield is 100clearly presented experimental evidence. Since the TD-LIF is the basis of all quantitation in this paper, relative sensitivity data for some representative species is certainly warranted. On page 6732, lines 14 and 27, and on page 6733, line 24, the issue of the NO2 yield is not even mentioned as one of the possible uncertainties. NO2 yield is now mentioned as a possible uncertainty which would bias branching ratios low. Until proof is shown that the NO2 yield is indeed 100%, then one could argue that this is the largest source of uncertainty. This issue could be resolved by either calibration of the CIMS independently for one or more of the pure compounds, and comparison of calibration factors, or through proof that the NO2 yield is 100% for all compounds in the carrier gas. Hopefully, this is readily achievable, or known, but not stated explicitly in the paper. ‘’

In the absolute yield experiments, the reviewer is correct in stating that HN concentrations were measured by the GC-TD-LIF. This instrument was periodically calibrated using an NO_2 standard (5ppm NO_2 in N_2), and evaluated with isopropyl nitrate, as discussed above. We agree with the reviewers concerns regarding the conversion of the HN to NO_2 and we discuss this uncertainty and its impact on the determination of the branching ratios in the revised manuscript.

‘’ I note that the analytical section on the calibration in Section 2.3 is a bit confusing, or not immediately apparent, in that the GC analysis is for a discrete sample in the form of a Gaussian peak, with a concentration in N2 that is continuously changing over the width of the peak; can you explain a bit more clearly how you convert the hopefully known integrated amount of RONO2 in that peak into a CIMS sensitivity in some units like Hz/ppt?"

We apologize for the lack of detailed explanation. To calculate the CIMS' sensitivity for a particular nitrate compound, specific peaks with the same elution time were integrated for the TD-LIF and CIMS instruments. The integrated TD-LIF peak has units of pptv × s, and the integrated CIMS peak has units of normalized counts × s. These are then divided to yield the CIMS sensitivity with units of normalized counts × pptv^{-1}.

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‘’1. I think the word "scatter" on page 6724, line 17 is not quite right. Within each of the existing literature data sets, the yields are not particularly scattered. Rather, for a particular peroxy radical (and you have to include this paper to even say this), the literature data cover a rather wide, conflicting range.”

Agreed. This discussion has been revised in the manuscript to be more clear.

‘’2. Page 6726, lines 306: what was the NOx concentration for the hydroperoxide yield measurements? Was it measured?”

The NOx concentrations in our ROOH yield experiments were below the detection limit (50 pptv) of our NOx analyzer. HN signals also provide a measurement for NO concentration in the chamber. For the set of experiments discussed below, no HN signals were measured during the hydroperoxides yield measurements (implying less than < 40pptv).

‘’Is it important that there are not multiple reaction paths available to the peroxy radicals? ‘’

The reviewer is correct in pointing out that there are multiple reaction pathways available to the peroxy radicals besides reaction with HO2 in our chamber experiment, and these are: $RO_2 + NO$, RO_2 H-shift self-isomerization, $RO_2 + RO_2$, and RO_2 + wall. $RO_2 + NO$ reactions would not disturb the ROOH isomeric distribution unless the RO2 + NO reaction rate differs between peroxy radicals. We did not detect products resulting from RO_2 H-shift isomerization, nor do we expect for these compounds to undergo H-shift isomerizations given the RO_2 lifetimes (estimated to be <1.0s) in these experiments. For similar reasons, RO_2 + wall is not expected to be a large contribution, as the mixing time of our chamber (approximately 5 minutes) is two orders of magnitude slower than the RO_2 lifetime.

$RO_2 + RO_2$ chemistry would perturb the ROOH isomeric distribution due to the strong dependence of peroxy radical rates on the alkyl substitution of R. We have conducted

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additional experiments to test our sensitivity to $RO_2 + RO_2$ chemistry in the revised manuscript. A set of propene ROOH isomer yield experiments were run where the ratio of HO_2 to RO_2 was increased by changing the initial alkene to hydrogen peroxide concentrations for a given light flux. Conditions where the propene hydroperoxide isomer yields reached a plateau were noted and isomer hydroperoxide yields of the remaining alkenes were measured at these conditions. This increased the minor product yield in all cases as expected. The revised results are shown below and included in the revised manuscript:

Propene (OH at C2: OH at C1)

revised - 40:60

original – 32:68

1-Butene (OH at C2: OH at C1)

revised – 35:65

original – 27:73

Methylpropene (OH at C2: OH at C1)

revised – 21:79

original – 11:89

2-methyl 2-butene (OH at C2: OH at C3)

revised: 31:69

original: 25:75

1-hexene (OH at C2: OH at C1)

revised: 30:70

original: 23:77

“Lines 21-22 - it is not clear why the amount of air in the chamber impacts conversion of NO to NO2 (in a positive way).”

The reaction NO + NO + O2 forms 2NO2. This reaction is dependent on the square of NO concentration. By adding NO when there is more air in the bag, the NO concentration is lower, and thus lowers the rate of dark conversion of NO to NO2.

“3. Page 6730 line 5, remove the word "of". Line 7 - define a and b. The sentence at the bottom of this page needs to be split into two sentences.”

Corrected.

“4. Page 6731, line 11, you should move the (Y=...) to after the word "yield", since this is the yield, not the ratio. “

Corrected.

“Line 22 - the loss was estimated iteratively, correct?”

The reviewer is correct, and the manuscript has been clarified.

“5. Page 6732, line 10 should say rate "constant", and the word "the" should precede "same". Line 18 - does the word "the" come after propene?”

Corrected.

“6. Page 6734, line 4 - by "scale" you mean linear fit?”

Yes, linear fit. This discussion has been expanded on in the text to be more clear.

“7. Page 6735, line 26, you need a - after the "methyl".” Corrected. “8. Page 6736, line 4 - explain how the transmission was measured.”

Transmission is measured by comparing the CIMS signal measured through the ‘direct sampling’ method (sampling only through a 1.5m Teflon line with <0.2s residence time) to the entire CIMS signal at a given m/z over the entire chromatogram. The ratio of these two quantities, taking into account the volume of gas sampled in each GC trapping period and the flow rate of the direct sampling, provides a transmission value for the GC method. This has discussion has been added to the text.

‘’Table 5 - can you provide uncertainties for the -OOH % isomer distribution? I note that the data in this Table represent highly valuable information, and they will become widely utilized once published, so the uncertainties are important.”

These uncertainties are now included in the manuscript in the expanded section on the ROOH isomer distribution. The revised manuscript has included a more complete discussion of the potential uncertainties in the distribution, and lists the various assumptions used to calculate isomer distributions.

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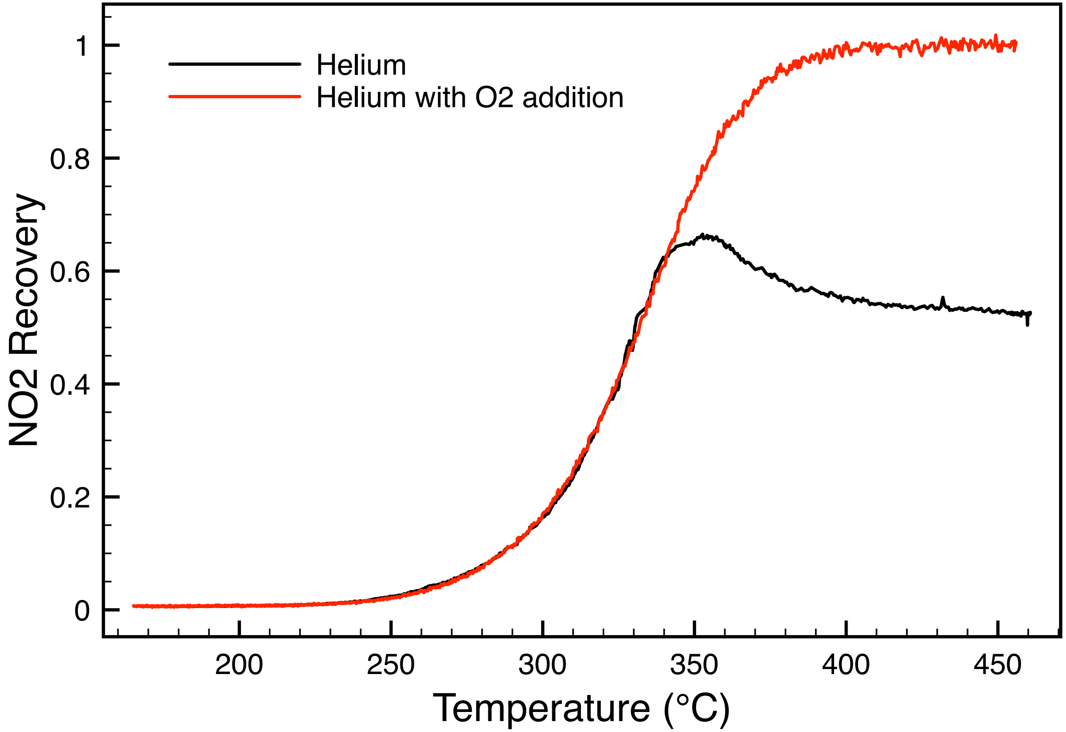
Helium
Helium with O2 addition
NO2 Recovery
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250
300
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Temperature (°C)

Fig. 1.

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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 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 1×10^{-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 3×10^7 molec cm^{-3}, and a seed to wall surface area ratio of 8.2×10^{-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 2.3×10^{-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.

References:

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Hydroxy nitrate production in the OH-initiated oxidation of alkenes

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Abstract. Alkenes ~~generally react rapidly~~ are oxidized rapidly in the atmosphere by addition of OH and subsequently O_2 ~~to form beta~~ leading to the formation of β hydroxy peroxy radicals. These peroxy radicals react with NO to form ~~beta~~ β hydroxy nitrates with a branching ratio α. We quantify α for C_2–C_8 alkenes at ~~296~~295 K ±3 and 993 hPa. The branching ratio can be expressed as ~~$\alpha = (0.042 \pm 0.008) \times N - (0.11 \pm 0.04)$~~ $\alpha = (0.045 \pm 0.016) \times N - (0.11 \pm 0.05)$ where N is the number of heavy atoms (excluding the peroxy moiety), and listed errors are 2σ. These branching ratios are larger than previously reported and are similar to those for peroxy radicals formed from H abstraction from alkanes. We find the isomer distributions of ~~beta~~ β hydroxy nitrates formed under NO-dominated peroxy radical chemistry to be ~~similar to~~ different than the isomer distribution of hydroxy hydroperoxides produced under HO_2-dominated peroxy radical chemistry. ~~With the assumption of~~ Assuming unity yield for the hydroperoxides ~~, this~~ implies that the branching ratio to form ~~beta hydroxy nitrates from primary, secondary, and tertiary~~ β hydroxy nitrates increases with substitution of RO_2 ~~are similar.~~

. Deuterium substitution enhances the branching ratio to form hydroxy nitrates in both propene and isoprene by a factor of ∼ 1.5. ~~These observations provide further evidence for importance of the ROONO lifetime in determining the branching ratio to form alkyl nitrates.~~

~~We use these measurements to re-evaluate the~~ The role of alkene chemistry in the Houston region is re-evaluated using the $RONO_2$ branching ratios reported here. Small alkenes are found to play a significant role in present day oxidant formation more than a decade (2013) after the 2000 Texas Air Quality Study identified these compounds as major contributors to photochemical smog in Houston. ~~We find that small alkenes play a larger role in oxidant formation than previously recognized.~~

1 Introduction

The formation of alkyl nitrates is an important process controlling tropospheric oxidants and the lifetime of NO_x. During day time, alkyl nitrates form via a ~~minor~~ radical chain terminating branch in the reaction of alkyl peroxy radicals with NO. The major branch in this chemistry recycles HO_x and produces ozone. The fate of alkyl nitrates is thought to be determined by either: (1) deposition leading to loss of atmospheric NO_x or (2) further reactions that lead to recycling of NO_x or conversion of the organic nitrates to HNO_3. Thus, $RONO_2$ can serve ~~as both~~ either as a permanent sink ~~, and~~ or as a transport mechanism for NO_x.

Alkyl nitrates also play an important role in organic aerosol formation (Rollins et al., 2012; Brown et al., 2009). Aerosol nitrates have been observed to form as a result of NO_3 chemistry, though our understanding of the gas phase mechanisms leading to aerosol nitrate remains incomplete.

Knowledge of the branching ratio of $RO_2 + NO$ to form alkyl nitrates from RO_2 derived from specific VOC is important for diagnosing the role of individual VOC in ozone and aerosol formation. This knowledge can then guide specific control strategies to mitigate pollution (Ryerson et al., 2003; Rosen et al., 2004; Farmer et al., 2011).

Many previous studies have ~~been conducted to determine the branching ratio~~ reported VOC-specific branching ratios to form alkyl nitrates~~from specific VOCs~~. These studies suggest that the branching ratios increase with increasing carbon number, increasing pressure, and decreasing temperature (Orlando and Tyndall, 2012 and references therein). This behavior has been interpreted as evidence that the lifetime of the O-ONO intermediate controls the fraction of the nascent complex that ~~follow the curve crossing to the~~ isomerizes onto the -ONO$_2$ surface. ~~This crossing~~ The dynamics that lead from the peroxynitrite (ROONO) to the nitrate (RONO$_2$) is, however, not well understood (Lohr et al., 2003; Barker et al., 2003; Zhang et al., 2002).

Alkenes react rapidly by addition of OH and ~~subsequently~~ O$_2$ to form ~~beta~~ β hydroxy peroxy radicals. These peroxy radicals react with NO to form ~~beta~~ β hydroxy nitrates. ~~We define the fraction of OH that adds to carbon n as f_{an} out of the total OH+alkene reaction. The total fraction of OH+alkene that proceeds via addition is given as $f_a = f_{a1} + f_{a2} + \ldots + f_{an}$. The total fraction of OH + alkene that proceeds via H-abstraction is given as $f_b = f_{b1} + f_{b2} + \ldots + f_{bn}$, where the subscript indicates the carbon at which H-abstraction takes place. Therefore $f_a + f_b = 1$. We define the branching ratio (α_n) to represent the fraction of R+NO reaction that produces RO, where the subscript n denotes the carbon alpha to the peroxy radical (Fig. 1). The isomer averaged branching ratio (α no subscript) to form beta hydroxy nitrates from OH addition to a mono-alkene is then defined in this paper as: $\alpha = f_{an} \times \alpha_{n+1} + f_{an+1} \times \alpha_n$.~~

~~Yields of hydroxy nitrates (Y_{HN}) are defined as the change in hydroxy nitrate concentration over the change in hydrocarbon (HC): $Y_{HN} = -d[HN]/d[HC]$. Isomer averaged branching ratios (α) to form hydroxy nitrates from hydroxy peroxy radicals can be calculated from beta hydroxy nitrate yields by normalizing for the fraction of the alkene reactions with OH that proceed via OH addition: $\alpha = Y_{HN}/(f_a/(f_a + f_b)) = Y_{HN}/f_a$. For alkenes studied here, f_a is greater than 0.75.~~

Previous studies have suggested that the branching ratio to form ~~beta~~ β hydroxy nitrates from reaction of ~~beta~~ β hydroxy peroxy radicals with NO is lower than ~~that~~ for peroxy radicals produced from reactions of alkanes of the same carbon number with OH (O'Brien et al., 1998). The lower nitrate branching ratios for ~~beta~~ β hydroxy peroxy radicals have been attributed to the ~~beta~~ β hydroxy group weakening the O-ONO bond, shortening the lifetime of the OONO complex toward decomposition to NO$_2$ ~~,~~ and thereby reducing the time available to sample the ~~curve~~ crossing to the ~~nitrates~~ nitrate surface (RONO$_2$) (Muthmuruthma et al., 1993; O'Brien et al., 1998; Matsunga and Ziemann, 2009, 2010). ~~This interpretation is clouded~~ Patchen et al. (2007), however, ~~by the large scatter in the measured yields of alkyl nitrates from alkenes. Several studies report~~ reported the branching ratio to form hydroxy nitrates derived from 1- and 2-butene as larger than previously reported by O'Brien et al. (1998). This study was conducted at 100 torr where RONO$_2$ yields should be smaller than at atmospheric pressure. Additional studies conducted on alkenes using long-path FT-IR have determined total alkyl nitrate yields similar to those ~~of the equivalent size alkane~~ determined for n-alkanes. However, these studies provide only upper bounds for branching ratios to RONO$_2$ due to the possible formation of organic nitrate from RO + NO$_2$ chemistry (Atkinson et al., 1985; Tuazon et al., 1998; ~~Patchen et al., 2007;~~ Aschmann et al., 2010)~~while others generally report yields $\sim 1/2$ as large (e. g. O'Brien et al., 1998). The wide distribution of measured nitrate yields may reflect the challenges in quantifying hydroxy nitrates. Consistent with this interpretation, lower nitrate yields were obtained using HPLC or GC methods while higher yields were found in experiments that used remote sensing (e.g. long-pass FTIR) or direct sampling techniques.~~ .

In this study, we use CF$_3$O$^-$ CIMS to quantify the hydroxy nitrates ~~formed during the OH oxidation of alkenes in the presence of and NO~~yield. In addition, we utilize gas chromatography with both CF$_3$O$^-$ CIMS and thermal dissociation NO$_2$ laser-induced fluorescence (TD-LIF) to resolve and quantify isomeric distributions of these hydroxy nitrates. The TD-LIF instrument provides independent confirmation that the observed signals are alkyl nitrates and enables ~~determination of the sensitivity of the CIMS instrument for the nitrates for which standards are not available. The combination of direct sampling and chromatographic separation demonstrates that losses of the hydroxy nitratesin our GC analysis are minimal, and provides confidence in the apportionment of isomer yields of the hydroxy nitrates~~secondary calibration of CF$_3$O$^-$ CIMS sensitivity by the TD-LIF for individual β hydroxy nitrates.

~~Here we describe the measurements of beta hydroxy nitrates from OH oxidation of alkenes, their branching ratios to formation, and their isomer distributions.~~

2 Materials and methods

1-propene [propene] (>99 %), d_6-propene (> 99 %), 1-butene [but-1-ene] (> 99 %), cis-2-butene [*cis*-but-2-ene] (> 99 %), methylpropene [2-methylpropene, isobutylene, isobutene] (> 99 %), 1-pentene [pent-1-ene] (> 98 %), 2-methyl 1-butene [2-methyl but-1-ene] (> 98 %), 2-methyl 2-butene [2-methyl but-2-ene] (> 99 %), isopropyl nitrate [nitric acid, 1-methylethyl ester] (> 99 %), 1-hexene [hex-1-ene] (> 99 %), 1-octene [oct-1-ene] (> 98 %), 1,2-butanediol [butane 1,2 diol] (> 98 %) purity were purchased from Sigma Aldrich and used without further purification. Hydrogen peroxide (30 % and 50 % by weight in water) was purchased from Sigma Aldrich. Ethene [ethylene] (> 99 %) was purchased from Scotty Specialty Gases. A nitric oxide [NO] (1994 ± 20 ppmv in ultra high purity N$_2$) standard gas tank for chamber experiments was prepared by Matheson. ~~A second nitric oxide~~ Nitrogen dioxide [~~NO~~NO$_2$] (5 ppmv in ultra high purity N$_2$) gas tank for TD-LIF calibration was prepared by Matheson. Methylnitrite (CH$_3$ONO) was synthesized, purified, and stored using methods similar to those described by Taylor et al. (1980).

2.1 Environmental chamber experiments

The CIMS and thermal dissociation laser-induced fluorescence instrument (TD-LIF) instruments and the ~~teflon~~ Teflon reaction chamber have been described previously (Crounse et al., 2013; Lee et al., 2014). Briefly, photochemical experiments were conducted in a 1 $\mathrm{m^3}$ enclosure composed of fluorinated ethylene propylene copolymer (Teflon-FEP, Dupont). UV photolysis of hydrogen peroxide (H_2O_2) or methyl nitrite (CH_3ONO) provided the primary HO_x source. Experiments to determine the hydroxy nitrate yields were typically conducted with initial mixing ratios of 0.08–2 ppmv of alkene, 0.2–2 ppmv (±10 %) of hydrogen peroxide or 40-200 ppbv methyl nitrite, and 0.5–4 ppmv (±5 %) of NO. Experiments to determine hydroxy hydroperoxide isomeric distributions were conducted with initial mixing ratios of ~~15–30~~2–30 ppbv alkene and ~~2~~2–20 ppmv of hydrogen peroxide. All experiments were performed at ambient pressure, approximately 993 hPa. Table ~~1~~ 41 provides a complete list of experiments.

Alkene or CH_3ONO addition to the environmental chamber was accomplished by first flushing a 500 $\mathrm{cm^3}$ glass bulb with the ~~alkene~~ compound and then filling it to the desired pressure (~~5–20~~1–20 hPa). The bulb was then filled with N_2 gas to 993 hPa. If required, the ~~alkene~~ compound was serially diluted by pumping the bulb down to the desired pressure (5–400 hPa) and backfilling again with N_2 to atmospheric pressure. The concentrations of ethene, propene, 1-butene, ~~cis-2-butene,~~ 2-methyl propene, 2-methyl ~~butene, and~~ 2-butene, 2-methyl 1-butene, 1-hexene ~~determined by pressure methods were verified by~~ and 1-octene were determined within the bulb by FT-IR spectroscopy. FT-IR cross sections were obtained from the PNNL database (Johnson et al., 2002; Sharpe et al., 2004) for all compounds except cis-2-butene and d_6-propene. Determinations of the concentrations of d_6-propene and cis-2-butene were based on manometry, and checked against GC-FID measurements relative to the other gases added in the same experiment assuming equivalent FID signal per carbon atom. These independent methods agreed to within 3 %. ~~Experimental conditions are listed in Table 3.~~

NO addition was accomplished by evacuating a 500 $\mathrm{cm^3}$ glass bulb, and filling from the standard tank to the desired pressure. NO was added to the enclosure only after at least 0.25 $\mathrm{m^3}$ of air was added to ~~avoid~~ lessen conversion of NO to NO_2 from the reaction of $2NO + O_2$. All pressure measurements were obtained using 13.3 hPa or 1333.3 hPa full scale absolute pressure gauges (MKS Baratron™). H_2O_2 addition was accomplished by evaporating a known mass of 30 or 50 % by weight H_2O_2 in water. Concentrations were confirmed by spectrometry.

The composition of the chamber was monitored by sampling from the enclosure at ∼ 2000 sccm through a single 4 mm ID perfluoroalkoxy line with instruments sampling in series: (1) ToF-CIMS (Tofwerk, Caltech), (2) Triple Quadripole MS-MS CIMS (Varian, Caltech), (3) GC-FID (HP 5890 II), (4) NO_x Monitor (Teledyne 200EU), (5) O_3 Monitor (Teledyne 400E). ~~The~~ Sampling conducted this way minimizes surface interactions by lowering the residence time of chamber air in the sampling line to <0.2s. The sampling configuration in which chamber air passes only through a Teflon sampling line without first entering a gas chromatograph is referred to here as 'direct' sampling. The specifics of the ~~ToF-CIMS and MS-MS~~ CIMS have been described in detail elsewhere (Crounse et al., 2006, 2011, 2012, 2013; Paulot et al., 2009; St. Clair et al., 2010). ~~The TD-LIF quantitatively converts alkyl nitrates to by thermal dissociation in a 400C oven. is then measured by laser-induced fluorescence (Lee et al., 2014).~~

Reaction products were monitored using CF_3O^- chemical ionization mass spectrometry (CIMS) methods. ~~Using cluster ion signals of $(M+85)$ m/z, where M is the molecular weight of the neutral species,~~ Multifunctional products from alkene oxidation were detected using CF_3O^- cluster ion signals observed at m/z $M+85$ product. The following m/z were used for hydroxy nitrate determination: ethene, 192; propene, 206; d_6-propene, 212; 1-butene/cis-2-butene/methylpropene, 220; 2-methyl,2-butene/1-pentene/2-methyl 1-butene, 234; 1-hexene 248; 1-octene, 276. For hydroxy hydroperoxides, the following m/z were used for quantification: propene, 177; 1-butene/methylpropene, 191; 2-methyl 2-butene, 205; 1-hexene, 219. 1,2 butanediol was monitored using signal at m/z 175, and the resulting hydroxycarbonyls were monitored m/z 173.

The alkene concentrations were monitored ~~by~~ using an GC-FID (Agilent 5890). Chamber air was sampled into a 10 $\mathrm{cm^3}$ stainless steel sample loop or a 30 $\mathrm{cm^3}$ PFA sample loop using a six-port valve. The sample was transferred to the head of the column in the oven at temperatures between 308–373 K, depending on the hydrocarbon. In the case of ethene, samples were cryotrapped with liquid nitrogen on the head of the column. A megabore (0.53 mm) 30 m Plot-Q column (JW Chemicals) was used to separate compounds using 7–9 $\mathrm{stdcm^3\,min^{-1}}$ N_2 carrier gas. A suitable temperature ramp was selected for each compound.

2.2 ~~Photooxidation~~

~~After addition of the reagents~~

2.1.1 GC-CIMS/LIF chromatography

After oxidation, the chamber air was ~~monitored for at least 20min to assure a well-mixed reactor. UV lights were then turned on, initiating photooxidation of hydrocarbon. The~~ analyzed using GC-CIMS/LIF (gas chromatography CF_3O^- ~~CIMS and GC-FID were used to monitor the reaction progress. For relative nitrate branching ratio experiments, we minimized the fraction of the hydrocarbon oxidized (<10) to~~

~~ensure that little of the nitrates are photochemically removed. Experiments were initiated at 293, and the temperature increased slowly 2–4after the lights were turned on. After an appropriate oxidation period, lights were turned off, and the contents of the bag were monitored for at least ten minutes to precisely determine the concentrations of the gas-phase products.~~

2.2 ~~Post-experiment GC-CIMS/LIF monitoring~~

~~Following each experiment, products were analyzed using gas chromatography. For each GC run, a controlled mass of air ranging from 200–2500was~~ CIMS/TD-LIF). Chamber air is pulled through a Teflon sampling line, through a Teflon 3-port valve, and cryofocused at 240–280 K on the head of a 4 m megabore HP 612, a 4 m megabore RTX-1701, or 1 m ~~RTX-1701 megabore column. Temperature ramping for every compound was :~~ megabore RTX-1701 column. Columns were held inside a Varian GC oven (CP-3800). Following the GC, the column effluent was split between the ToF-CIMS instrument and the TD-LIF system for the experiments listed in Table 41. For all other experiments where the TD-LIF instrument was not used, the column effluent flowed directly to the ToF-CIMS. After a measured flow of chamber air ranging from 30–200 std cm^3 was cryofocused over a length of time ranging from 2–12 min by placing the GC column in a cooled (-20 °C) isopropanol bath, the three-port valve was switched to allow carrier gas (N_2) to flow through the GC column. The volume of chamber air cryofocused in this manner was determined by the collection time and the flowrate (inferred from manometry). Carrier gas flow was controlled by a mass flow controller (MKS) at 8.7 std cm^3 min^{-1} N_2. Temperature program (30 °C, hold 0.1 min, 3 °C min^{-1} from 30–60 °C, 10 °C min^{-1} to 130 °C, hold 3 min~~. Carrier gas flow was constant and set by a mass flow controller (MKS) to be 8.7~~) started approximately 2-3 minutes after cryofocusing. All wetted surfaces in the analytical setup were comprised of Teflon, PEEK, or GC column materials to limit surface interactions.

~~Following the GC , the column effluent was split and directed to both the ToF-CIMS instrument and to the~~ The TD-LIF ~~system.~~ system sampled a portion of the GC carrier gas into 400 °C oven. Pure O_2 is added to this flow upstream of the TD oven to ensure complete converson of $RONO_2$ to NO_2. NO_2 is measured using laser-induced fluorescence (Lee et al., 2014). The system was calibrated at the same operating pressure with a standard tank of NO_2. The conversion efficiency of the TD-LIF was evaluated with isopropyl nitrate and found to be 100% (see Appendix B). We assume here that conversion of other $RONO_2$ is also 100%. To the extent the conversion of these hydroxy nitrates to NO_2 is less than 100%, the reported branching ratios are biased low.

The ToF-CIMS instrument was operated in the same manner as during the photochemistry with diluted column effluent substituting for the ambient flow. With this split flow configuration, the concurrent elution of alkyl nitrates was monitored by both the ToF-CIMS and TD-LIF instruments, enabling ~~absolute~~ secondary calibration of the CIMS sensitivity by the TD-LIF to the individual alkyl nitrates. ~~Following each photochemistry experiment, at least three replicate GC runs were conducted. To determine transmission through the GC, the integrated CIMS signal at the appropriate m/z from the GC effluent was compared to direct sampling measurement of the same m/z. For hydroxy hydroperoxide experiments and relative nitrate yield experiments, no TD-LIF measurement was used.~~

The determination of the split ratio (approximately 10 : 1) between the CIMS and TD-LIF NO_2 instrument was performed using an isopropyl nitrate standard (80 ppbv in air) prepared in the same fashion as the alkenes described above. The gas standard was both directly sampled from the chamber and following cryo-collecting $\sim 200\,\mathrm{cm}^3$ on an HP 612 column and eluting the peak in the usual GC configuration. The signal level in the TD-LIF instrument was recorded as the GC ramped through its usual temperature program. Signal levels were also compared between direct measurement of ∼ 80 ppbv isopropyl nitrate within a Teflon bag into the TD-LIF system and collecting for four minutes on a cooled sample loop. A separate check was also conducted with prepared standards of isoprene hydroxy nitrates in which the standard was directly sampled from the chamber and through the GC system. This measurement was problematic due to long equilibration times (>3 hours) resulting from low sampling flow limited by the small diameter tubing in the TD-LIF optimized for GC use. The TD-LIF was also calibrated at the end of each photochemistry experiment with gas standard of 5 ppmv NO_2 in N_2 (Matheson) under matching pressure conditions.

3 ~~Results and discussion~~

~~In this section, we proceed through the following analysis~~

2.0.1 Experiments to determine hydroxy nitrate branching ratios relative to propene

Experiments 31-36 (Table 41) were conducted to determine the β hydroxy nitrate yields from alkenes relative to the β hydroxy nitrate yield from propene. These experiments involved simultaneous oxidation of up to 6 alkenes. Initial alkene concentrations were determined by FT-IR spectroscopy. The chamber was monitored for at least 20 minutes to determine the background signals. UV lights were turned on for a period (<10 min) sufficient to achieve a hydroxy nitrate concentration high enough for quantification while minimizing secondary OH losses of hydroxy nitrates. Less than 10% of each alkene species was oxidized in each experiment. Experiments were initiated between 292 and 293 K and the temperature rise was no more than 1 K over the course of the experiments. Hydroxy nitrate branching ratios were determined relative to those of propene with the exception of Experiment 31, which measured d_6-propene hydroxy nitrate branching ratios relative to 1-butene. Accurate GC-FID quantification in these experiments was not possible due to the small change in concentration of each compound.

2.0.2 Experiments to determine hydroxy nitrate branching ratios in an absolute manner

Experiments 1-19 (Table 41) were conducted to determine the absolute branching ratios to form β hydroxy nitrates. Experiments involved addition of 1-3 alkenes, NO, and H_2O_2 or CH_3ONO into the chamber. Initial alkene concentrations were determined by FT-IR and confirmed by manometry and GC-FID peak areas. Isoprene hydroxy nitrates or isoprene hydroxy hydroperoxides were also added to the chamber in Experiments 1-7 to measure their OH rate constants relative to propene as described in experiments of Lee et. al, 2014 and St. Clair et al.(in preparation). To measure OH exposure, 1,2 butane diol (a reference compound measurable by CIMS) was added to a series of experiments to confirm the alkene decay measured by GC-FID. In these experiments UV lights were turned on until a significant and quantifiable decay of hydrocarbon was observed (>15%) on the GC-FID. Experiments were initiated between 292 and 293 K, and the temperature increased by at most 7 K after the lights were turned on.

2.0.3 Experiments to determine hydroxy hydroperoxide isomer distributions

Experiments 20-30 (Table 41) were conducted to determine the hydroxy hydroperoxide isomer distributions. Experiments involved addition of 1-3 alkenes and H_2O_2. Initial alkene concentrations were determined by FT-IR spectroscopy. UV lights were turned on until a measurable concentration of hydroxy hydroperoxides was produced. Less than 10% of each alkene species was oxidized in each experiment as indicated by GC-FID signal areas.

2.0.4 Post-experiment GC-CIMS/TD-LIF monitoring

Following each experiment, products were analyzed by GC-CIMS/TD-LIF or GC-CIMS. At least three replicate GC runs were conducted. Transmission through the CIMS portion of the GC-CIMS/TD-LIF was measured by comparing the direct sampling measurement to the integrated chromatogram signal for a given m/z. The integrations were corrected by blank GC runs (less than 3% signal in all cases over the elution time of the hydroxy nitrate peaks). The transmission was determined by the ratio of the direct sampling and the total chromatogram signals after taking into account the sampling flowrate differences.

3 Results and discussion

The following analysis procedure was used to calculate branching ratios from the experimental data:

1. ~~We estimate the~~ β hydroxy nitrate CIMS sensitivites are determined from simultaneous measurement of hydroxy nitrates by cryofocused gas chromatography.

2. The fraction of the reaction of OH that proceeds via addition, f_a, is estimated from previously reported kinetic data on alkenes. This allows ~~us to normalize~~ normalization of subsequent measurements of ~~Y_{HN}~~ the yields of β hydroxy nitrates, $Y_{\beta HN}$, to produce branching ratios, α.

3. ~~We determine branching~~ Branching ratios to form hydroxy nitrates, α, from alkenes relative to $\alpha_{HN\_propene}$ ~~. This method allows us to determine the most internally precise~~ are determined through experimental data. These results allow direct comparison of the dependence of α ~~while oxidizing only a small fraction of the alkene, thereby avoiding the complication of secondary chemistry. We measure the absolute branching ratios,~~ on structure. α ~~, of a subset of compounds. We find that the branching ratios are~~ is well described by a linear relationship: $\alpha = m \times N + b$, where α is isomer-averaged branching ratio, and N is the number of heavy atoms in the peroxy radical (not counting the peroxy radical oxygens).

4. ~~We~~ The absolute branching ratios, α, are determined using absolute quantification of alkene and hydroxy nitrate concentrations. The dependence of α on the number of heavy atoms, N, is derived.

5. The entire absolute branching ratio dataset is used to place all relative nitrate branching ratios on an absolute basis~~using the relationship derived in (3)~~.

6. ~~We determine specific isomer~~ Isomer specific distributions for alkenes ~~using the~~ are derived using GC chromatograms of hydroxy nitrate isomers.

7. ~~We infer~~ The OH addition branching ratios ~~by analyzing GC chromatograms of hydroxy hydroperoxides from alkenes~~ are inferred by analyzing hydroxy hydroperoxide isomer distributions of alkenes oxidized by OH under HO_2 dominated conditions.

8. ~~We determine the~~ The dependence of the alkyl nitrate branching ratios on the type (i.e., primary, secondary or tertiary) of ~~beta~~ β hydroxy RO_2 radicals are determined by comparing (5) and (6).

3.1 ~~Normalizing nitrate yields for H-abstraction~~

~~To calculate~~

We define the branching ratio ~~for reaction~~ (α_n) to represent the fraction of RO_2~~with NO to form of beta hydroxy nitrates following addition of OH and to alkenes, it is necessary to estimate the fraction of the chemistry~~ + NO reaction that produces $RONO_2$, where the subscript n denotes the carbon alpha to the peroxy radical (Fig. 42). We define the fraction of OH that adds to carbon n as $f_{\mathrm{a}n}$ out of the total OH + alkene reaction. The total fraction of OH + alkene that proceeds via ~~OH addition ($f_\mathrm{a}/(f_\mathrm{a}+f_\mathrm{b})) = f_\mathrm{a}$. A quantitative determination of f_b from our experimental data is not possible because CIMS is insensitive to simple carbonyl or nitrate compounds. There have been few studies of~~ addition is given as $f_\mathrm{a} = \sum_{n=1}^{l} f_{\mathrm{a}n}$. The total fraction of OH + alkene that proceeds via H-abstraction ~~from alkenes by OH at ambient temperatures. The~~ is given as $f_\mathrm{ab} = \sum_{n=1}^{l} f_{\mathrm{ab}n}$, where the subscript indicates the carbon at which H-abstraction ~~channel by OH has been measured for propene and cis-2-butene to be less than 3, and for 1-butene to be 8 ± 3(Krasnoperov et al. , 2011; Loison et al. , 2010 and references therein). Aschmann and Atkinson (2008) measured OH rate constants for a series of 1-alkenes and found that the OH rate constant increases per additional Cgroup was 2×10^{-12}, roughly 25higher than the empirically derived increase in OH rate constant per additional Cgroup for n-alkanes (1.4×10^{-12}, Kwok and Atkinson, 1995)~~takes place. Therefore $f_\mathrm{a} + f_\mathrm{ab} = 1$. The isomer-averaged branching ratio (α no subscript) to form β hydroxy nitrates from OH addition to a mono-alkene is then defined in this paper as: $\alpha = f_{\mathrm{a}n} \times \alpha_{n+1} + f_{\mathrm{a}n+1} \times \alpha_n$. ~~Theoretical work by Pfrang et al. (2006a, b) has predicted that the chain length should not affect the rate of OH additionto 1-alkenes, which implies the increase in rate constant from 1-butene to 1-octene is attributable to the H-abstraction channels. Using this additivity relationship, the abstraction fraction (f_b) for 1-octene is calculated to be 28. For this analysis, we assume that f_b is 8for 1-butene and that the abstraction rate increases 1.4×10^{-12}per additional group as suggested by Kwok and Atkinson (1995), as non-allylic Cgroups are expected to be similar to Cgroups in alkanes. This calculation suggests 15H-abstraction for 1-hexene, and 22for 1-octene.~~

~~To estimate abstraction rates for methyl-substituted alkenes, we use an overall k_OH of $1.4 \times 10^{-12}$for 1-butene (Atkinson and Arey, 2003), Kwok and Atkinson's (1995) suggested k_OH for a CH_3 group of 0.14×10^{-12}, and an 8~~Yields of β hydroxy nitrates ($Y_{\beta\mathrm{HN}}$) are defined as the change in hydroxy nitrate concentration over the change in hydrocarbon (HC): $Y_{\beta\mathrm{HN}} = -\mathrm{d[HN]}/\mathrm{d[HC]}$. Hydroxy nitrates produced via H-abstraction ~~(f_b). We estimate an $k_\mathrm{OH,abstraction}$ rate constant for a secondary allylic hydrogen of 2.4×10^{-12}. Using an overall k_OH of $26.3 \times 10^{-12}$for propene (Atkinson and Arey, 2003) and an upper limit of 3abstraction, we derive an upper limit $k_\mathrm{OH,abstraction}$ rate constant of primary allylic hydrogen of 0.8×10^{-12}. Assuming vinylic hydrogen abstraction rates are negligible, we estimate f_b for cis-2-butene, methylpropene, and 2-methyl 2-butene to all be< 3.~~and subsequent alkoxy H-shift isomerization result in molecules with different molecular weights from hydroxy nitrates produced by OH addition, and therefore only β hydroxy nitrates produced via OH addition are counted in yields. Isomer averaged branching ratios (α) to form β hydroxy nitrates from β hydroxy peroxy radicals can be calculated from β hydroxy nitrate yields by normalizing for the fraction of the alkene reactions with OH that proceed via OH addition: $\alpha = Y_{\beta\mathrm{HN}}/(f_\mathrm{a}/(f_\mathrm{a}+f_\mathrm{ab})) = Y_{\beta\mathrm{HN}}/f_\mathrm{a}$. For alkenes studied here, f_a is greater than 0.75.

3.1 Determination of CIMS sensitivities by TD-LIF for hydroxy nitrates

CIMS sensitivities were derived from cryofocused gas chromatography and simultaneous measurement of β hydroxy nitrate compounds by CF_3O^- CIMS and TD-LIF. Discrete gaussian peaks which eluted at the same time in the CIMS and TD-LIF were integrated. The time integrated normalized ion counts from the CIMS was multiplied by the split ratio between TD-LIF and CIMS instruments then divided by the integrated NO_2 signal (ppbv × s) measured by the TD-LIF to determine a sensitivity in normalized counts ppbv of $RONO_2$. Sensitivities are listed in Table 42. An example chromatogram of GC-CIMS/TD-LIF from which sensitivities are derived is shown in Fig. D.

3.2 The relative yields of β hydroxy nitrates from alkene oxidation

~~All~~ β hydroxy nitrate branching ratios were measured relative to $\alpha_\mathrm{HN\_propene}$ for Experiments 31-36 with the exception of Experiment 31 which measured d_6-propene relative to 1-butene. With minimal oxidation of total hydrocarbon (< 10 %), the measured CIMS signal of each compound ~~can be~~ is used to determine the ratio of the yield of ~~hydroxy nitrates (~~β hydroxy nitrates, where yield is defined as $Y = f_\mathrm{a1} \times \alpha_2 + f_\mathrm{a2} \times \alpha_1$~~):~~:

$$\frac{Y_\mathrm{HN\_alkene}}{Y_\mathrm{HN\_propene}} = \underline{\frac{\text{CIMS\_signal}_\mathrm{HN\_alkene}}{\text{CIMS\_signal}_\mathrm{HN\_propene}}} \frac{\text{signal}_\mathrm{HN\_alkene}}{\text{signal}_\mathrm{HN\_propene}} \times \underline{\frac{\text{sensitivity}_\mathrm{HN\_pro}}{\text{sensitivity}_\mathrm{HN\_alk}}}$$

$$\times \underline{\frac{[\text{propene}]_\text{average}}{[\text{alkene}]_\text{average}}} \frac{[\text{propene}]_\text{avg}}{[\text{alkene}]_\text{avg}} \qquad (1)$$

To determine the ratio of the ~~branching ratios~~average branching ratios ($\alpha_{alkene}/\alpha_{propene}$), we multiply the ratio of the yields by the ratio of the fraction of OH addition (f_a):

$$\frac{\alpha_{\mathrm{HN\_alkene}}}{\alpha_{\mathrm{HN\_propene}}} = \frac{Y_{\mathrm{HN\_alkene}}}{Y_{\mathrm{HN\_propene}}} \times \frac{f_{\mathrm{a\_propene}}}{f_{\mathrm{a\_alkene}}} \tag{2}$$

~~Average~~ The mean concentrations throughout the experiment were calculated by averaging the initial and final alkene concentrations. The amount of alkene oxidized could not be accurately determined by GC-FID due to the small fractional change ~~. Therefore~~ in the mixing ratio. Therefore, the loss was estimated iteratively by using the calculated branching ratio for the hydroxy nitrates (see Sect. ~~3.2~~ 3.3 for derivation of absolute branching ratios used in this calculation). The difference in the determination of ~~Y_{HN}~~ $Y_{\beta\mathrm{HN}}$ between using average vs. the initial alkene concentrations was less than 5 % in all cases. CIMS ~~signal measurements can be seen in Fig. 2.~~

~~Error in the estimate of the hydroxy nitrate branching ratios relative to $\alpha_{\mathrm{HN\_propene}}$ from Eq. (2) are therefore determined solely by the relative errors associated with the direct sampling CIMS measurement, the ratio of the estimated OH reaction rates, errors associated with determining the relative initial concentrations, and, in the case of secondary loss, the relative ratio of the loss rates.Relative errors in the k_{OH} rate constants were taken from Atkinson et al. (1983, 1986), and Aschmann and Atkinson (2008), and are reported to be<5. The k_{OH} rate for d_6-propene was assumed to be same as $k_{\mathrm{OH}}$for propene (Stuhl et al., 1998). PNNL spectral database IR cross sections were used to determine alkene gas concentrations, with an associated error of 2. For compounds with no published IR cross sections, the GC-FID signal was used to corroborate the pressure measurement. This contributes an additional 3error. Errors in the CIMS quantification of hydroxy nitrates include background signal subtraction, signal to noise level, and time lag associated with lower volatility compounds. The combination of these errors are estimated to be lower than 10for all compounds. Additional uncertainty in sensitivity for d_6-propene 1-octene hydroxy nitrates, compounds which were not calibrated by using TD-LIF, was assumed to be 3.~~ signals from Expt. 19 are shown in Fig. 43. Estimates for secondary loss of hydroxy nitrates by reactions with OH for the relative yield experiments (k_{OH} estimates ~~primarly~~ from Treves and Ruddich, 2003 and ~~sealed by~~ Kwok and Atkinson, 1995) using the method described by Atkinson et al. (1982) result in corrections of <3 % and are neglected in this subset of experiments. For absolute yield determinations which involved larger OH exposure, the applied corrections are listed in Table ~~3.~~ 43.

~~To determine the relative nitrate yield, absolute sensitivities were derived from cryofocused gas chromatography and simultaneous measurement of hydroxy nitrate compounds by CIMS and TD-LIF. The~~ The relative branching ratio dataset allows us to directly compare the dependence of α on structure by reducing the uncertainties associated with the measurement and analysis. The analysis of the relative yield experiments also reduces systematic uncertainty through cancellation of correlated errors associated with ~~this determination include: the split ratio of eluent flow between the~~ determination of total chamber volume and the use of the GC-FID. The relative yield determination relies on the ratio of OH rate constants, the ratio of initial alkene concentrations, the ratio of CIMS HN sensitivities, and the ratio of CIMS HN signals. In each relative yield determination, only the ratio of OH rate constants and ratio of HN sensitivities are determined outside the given experiment.

3.3 Normalizing nitrate yields for H-abstraction

To calculate the branching ratio for reaction of RO_2 with NO to form β hydroxy nitrates following addition of OH and O_2 to alkenes, it is necessary to estimate the fraction of alkene loss, f_a, that proceeds via this channel. A quantitative determination of f_a from our experimental data is not possible because CF_3O^- ~~CIMS and TD-LIF, absolute sensitivity to in the TD-LIF, and integration errors associated with determining a baseline for trailing peaks in both the CIMS and~~ CIMS is insensitive to singly functionalized carbonyl or nitrate compounds formed from the OH H-abstraction channels. The H-abstraction channel by OH has been measured for propene and cis-2-butene to be less than 3 %, and for 1-butene to be 8 ± 3 % (Krasnoperov et al., 2011; Loison et al., 2010 and references therein). There have, however, been few studies of H-abstraction rates for other alkenes at ambient temperatures.

Using theoretical methods, Pfrang et al. (2006 a,b) predicted that the ~~TD-LIF chromatograms. Combined errors for the split flow ratio and absolute determination are 10. Reproducibility of sensitivity from repeat chromatograms had errors than~~ chain length should not affect the rate of OH addition to 1-alkenes, and therefore, the increasing abstraction rate with size should scale with additional CH_2 groups.There is, however, disagreement in experimental results about how much the abstraction rate increases with each additional CH_2. Aschmann and Atkinson (2008) measured OH rate constants for a series of 1-alkenes and found that the OH rate constant increases at a rate of 2×10^{-12} ~~<5~~$\mathrm{cm^3\,molec^{-1}\,s^{-1}}$per CH_2 group, roughly 25 % ~~, except for propene (<15~~higher than for n-alkanes ($1.4 \times 10^{-12}\ \mathrm{cm^3\,molec^{-1}\,s^{-1}}$, determined by Kwok and Atkinson, 1995). For this analysis, we assume that f_{ab} is 8 % ~~)~~for 1-butene and, ~~which was signal-to-noise limited. It is possible that co-eluting compounds detectable in the TD-LIF but not~~ because H-abstraction from non-allylic CH_2 groups is expected to be similar to CH_2 groups in alkanes, we assume that the abstraction rate increases according to the ~~CIMS would bias the CIMS sensitivity low.For hydroxy nitrates from d_6-propene and1-octene, the CIMS measurement was assumed to have the same absolute sensitivity as hydroxy nitrates from propene and~~

parameterization suggested by Kwok and Atkinson (1995). This implies 15 % H-abstraction for 1-hexene~~respectively. These were estimated to have an additional uncertainty of 3~~, and 22 % for 1-octene. Using a rate similar to that reported in Aschmann and Atkinson (2008), the abstraction fraction (f_{ab}) for 1-octene would be 28 %. ~~Sensitivities are listed in Table 2. An example chromatogram of GC-CIMS/TD-LIF from which sensitivities are derived is shown in Fig. 3.~~

To estimate abstraction rates for methyl-substituted alkenes, we use an overall k_{OH} of $31.4\times10^{-12}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$ for 1-butene (Atkinson and Arey, 2003). Kwok and Atkinson's (1995) suggested k_{OH} for a CH_3 group of $0.14\times10^{-12}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$, and an 8 % H-abstraction (f_{ab}). We estimate a $k_{OH,abstraction}$ rate constant for a secondary allylic CH_2 group of 2.4×10^{-12}. Using an overall k_{OH} of $26.3\times10^{-12}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$ for propene (Atkinson and Arey, 2003) and an upper limit of 3 % abstraction, we derive an upper limit $k_{OH,abstraction}$ rate constant of a primary allylic CH_3 group of $0.8\times10^{-12}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$. Assuming vinylic hydrogen abstraction rates are negligible, we estimate f_{ab} for cis-2-butene, methylpropene, 2-methyl 1-butene, 2-methyl 2-butene to all be less than 5 %.

3.4 Absolute ~~beta~~ β hydroxy nitrate yields and branching ratios

~~An~~ The absolute yield of hydroxy nitrates for several of the alkenes was determined in ~~experiments that proceeded beyond 10alkene loss. The longer reaction time was necessary in order to quantify~~Experiments 1-19. Longer reaction times were necessary to quantify, with sufficient precision, the amount of alkene oxidized. The concentration of hydroxy nitrates at the end of the experiment was determined by measuring the total ~~TD-LIF~~ GC-TD-LIF peak signal which corresponded to a CIMS hydroxy nitrate signal. The initial concentration of alkene was determined by FT-IR and GC-FID, and total loss was determined by the ~~fractional~~ decay in peak area by the GC-FID. ~~The yield was then~~ In Experiments 11-14, 1,2 butanediol was also added as a reference compound to allow the total loss of alkene to be determined independent of the GC-FID. 1,2 butane diol was monitored using the CIMS at signal m/z 175 by CIMS to determine its decay over time. The ratio of the OH rate constants for 1,2 butanediol to propene is estimated to be 1.1 ± 0.1 from relative rate information from the literature (Atkinson et al., 1982, 1986; Bethel et al., 2001). The alkene decay inferred from the 1,2 butanediol decay was found to match the GC-FID alkene decay within error. The nitrate yield is calculated by dividing the ~~concentration~~ amount of hydroxy nitrates formed by the ~~loss of alkenes .~~ amount of alkenes reacted.

For each reaction, a ~~-~~secondary loss correction factor, F, was applied to account for losses of hydroxy nitrates by OH ~~(~~and wall loss using equations derived in Atkinson et al., 1982~~) using rate coefficients~~ , and substituting k_7 by $k_7\times$ OH and k_{10} by $k_{10}\times$ OH $+k_w$, where k_w is the experimentally derived first order wall loss rate constant. Rate coefficients for OH + hydroxy nitrates were estimated based on Treves and Ruddich (2003). ~~Errors include those associated with determining initial alkene concentration, determining final alkene concentration, determining the split ratio between the CIMS and TD-LIF, and the absolute calibration of the TD-LIF.~~ First order wall loss rate constants were determined by monitoring post-oxidation dark decay over at least an hour and found to be $\leq10^{-5}\mathrm{s^{-1}}$ for all compounds. A second correction factor, F_{temp}, was applied to normalize the yields to a single temperature (T = 293K) to account for the dependence of the branching ratio on temperature. F_{temp} was estimated using the temperature dependence on branching ratio described in Arey et al. (2001).

Branching ratios to form ~~beta~~ β hydroxy nitrates were ~~then derived from beta hydroxy nitrate yields by normalizing by~~ calculated by normalizing the β hydroxy nitrate by the fraction of OH + alkene reactions ~~that proceeds~~ estimated to proceed via OH addition ($\alpha=Y/f_a$). See Sect. 3.4 for more details ~~. Tabulated values are listed in Table 3. In Fig. 4, we show the dependence of the branching ratio on~~ (Table 43). The yields increase linearly with size of the molecule.

We find that the branching ratios can be expressed as $\alpha=(0.045\pm0.016)\times N-(0.11\pm0.05)$, where N is the number of heavy atoms in the peroxy radical ~~.~~ (not including the peroxy radical oxygens). The α derived for 2-methyl 2-butene was not included in the fit, as it was found to be significantly lower than 1-pentene and 2-methyl 1-butene. Preliminary data from other experiments (not reported here) indicate that α for another internal alkene, 2,3-dimethyl 2-butene, is also substantially lower than similar carbon number compound 1-hexene. It is unclear why these internal alkenes exhibit significantly lower branching ratios to form alkyl nitrates.

3.5 ~~Absolute hydroxy~~ Hydroxy nitrate branching ratios from relative measurements

To place the relative nitrate yields of the alkenes (3.2) on an absolute basis, we scale the slope of the error weighted fit of the relative branching ratios ~~by the~~ to match that of the slope of the error weighted fit derived from the observed dependence of the absolute branching ratios on N derived in Sect. 3.3. Branching ratios to form ~~beta~~ β hydroxy nitrates calculated using this method are listed in Table ~~4~~ **??** and shown in Fig. ~~5.~~ 45.

~~Our~~ The method of placing the relative branching ratios on an absolute basis are prone to correlated errors if the two data sets are not independent of each other. We believe the data sets are sufficiently independent for the following reasons: (1) the absolute nitrate yields require a ~~secondary loss by OH correction whereas the second~~ correction for OH, temperature, and wall loss whereas the relative set does not, (2) the determination of Δalkene relies on GC-FID for ~~one set and~~ the absolute data set while only initial reactant concentration and literature k_{OH} rate constants for the ~~other~~ relative set, (3) the ~~yield of beta hydroxy nitrates are determined by GC-TD-LIF in the absolute yield experiments, and are determined by direct sampling ToF-CIMS measurements and GC-CIMS, (4) most of the deviations from the fits (Figs. 4 and 5) are not correlated (i. e. only 2-methyl 2-butene is consistently lower than the linear fit).~~ deviations of the data from the best fit relationships are not well correlated. The two data sets, however, are prone to similar biases in the following ways: (1) initial alkene concentrations were measured by FT-IR and with the same reference spectra in both sets of experiments, (2) sensitivities for ~~beta hydroxy nitrate and absolute beta hydroxy nitrates~~ β hydroxy nitrates and absolute β hydroxy nitrate yields both rely upon GC-TD-LIF data.

As shown in Fig. 45, the dependence of the hydroxy nitrate branching ratios from β hydroxy peroxy radicals on the number of heavy atoms are similar to those observed for peroxy radicals derived from n-alkanes (Arey et al., 2001). This suggests that destabilization of the O-ONO bond due to the presence of the β hydroxy group is likely small.

Deuteration also leads to an increased branching ratio to form nitrates, possibly due to increased O-ONO lifetime resulting from the lower frequency vibrational and rotational modes. The nitrate branching ratio of d_6-propene is a factor of 1.5 times higher than h_6-propene. A similar increase in nitrate branching ratio has been observed for deuterated isoprene (Crounse et al., 2011).

The measured branching ratios to form ~~beta~~ β hydroxy nitrates (Table ~~4~~**??**) are consistent with Tuazon et al. (1998) ~~FT-IR determination for the formation~~ determinations of total alkyl nitrates ~~for~~ formed from methylpropene, cis-2-butene, and 2-methyl,2-butene. ~~They~~ For the experimental conditions in Tuazon et al., however, formation of methyl nitrate from $\mathrm{CH_3O + NO_2}$ may be significant. As the FT-IR nitrate determination includes the sum of all $\mathrm{RONO_2}$ species, these results represent an upper limit to the alkene-derived HN yield. Branching ratios reported here are also consistent with those reported by Patchen et al. (2007) ~~measured yields~~ for 1-butene and 2-butene determined by CIMS and calibrated using synthesized standards. ~~Our branching ratios are, however,~~

The measurements of the branching ratios reported here are significantly higher than those determined by O'Brien et al. (1998) using gas chromatography ~~. While the FT-IR determines the sum of all nitrate-containing compounds and the measurements presented here and by~~ with calibration using authentic standards. O'Brien et al. (1998) ~~comprise only hydroxy nitrate isomers, the difference between the two quantities is expected to be quite small for the studied alkenes . Reasons for these discrepancies are not clear but may reflect losses in the chromatographic analyses.~~

~~As shown in Fig. 5, the hydroxy nitrate branching ratios from beta hydroxy peroxy radicals on a per heavy atom basis are similar to those observed for peroxy radicals derived from n-alkanes as measured by Arey~~ used a similar GC separation technique followed by thermal dissociation of alkyl nitrates with detection of $\mathrm{NO_2}$ by chemiluminescence. The experimental conditions were quite different than the current study. Initial alkene and oxidant concentrations were two to three orders magnitude higher for most alkenes studied. Based on simulations of the experiments reported in O'Brien et al. (~~2001). This suggests that destabilization of the O-ONO bond due to the presence of the beta hydroxy group is likely small. Deuteration also leads to an increased branching ratio to form nitrates, possibly due to increased O-ONO lifetime resulting from the lower frequency vibrational and rotational modes. The nitrate branching ratio of d_6-propene is 50higher than h_6-propene. A similar increase in nitrate branching ratio has been observed for deuterated isoprene (Crounse~~ 1998), the high initial NO concentrations led to rapid production of copious amounts of $\mathrm{NO_2}$, which, upon UV illumination forms significant levels of $\mathrm{O^3P}$ for all experiments with initial $\mathrm{NO_x}$ concentrations >100ppmv. Our simulations suggest that significant alkene loss in their study was due to oxidation by $\mathrm{O^3P}$. This implies a significant underestimation of the branching ratios in the O'Brien et al.~~, 2011) .~~ (1998) study for all compounds derived from high $\mathrm{NO_x}$ experiments. See supplementary materials for further details on this analysis.

3.6 Nitrate yields from alkoxy isomerization

In addition to the ~~beta~~ β hydroxy nitrates, dihydroxy nitrates ~~form from those alkenes~~ are formed from β hydroxy alkoxy radicals that are able to undergo 1,5 H-shift chemistry ~~from the alkoxy radical~~ (Fig. ~~6~~46). The CIMS sensitivities for these nitrates could not be obtained because they had low transmission through the gas chromatograph. From ambient sampling, the CIMS signal for the dihydroxy nitrates, relative to the ~~beta~~ β hydroxy nitrates, are: 1-butene, $< 2\,\%$, 1-hexene, $> 10\,\%$, 1-octene, $> 5\,\%$. For 1-butene, an upper limit is provided due to the small amount formed. For the dihydroxy nitrates from 1-hexene and 1-octene, only lower limits are reported as significant uptake to the walls of the chamber was observed.

3.7 Hydroxy nitrate isomer attribution

An example GC chromatogram is shown in Fig. ~~7.~~ 47. Transmission through the GC was measured by integrating the entire chromatogram for a given m/z, dividing by direct sampling signal at that same m/z, and multiplying by the ratio of the direct sampling flowrate to the cryofocused gas volume. The transmission for all hydroxy nitrate isomers through the GC-CIMS/TD-LIF was measured to be 100 % ± 5 % except for 1-octene hydroxy nitrates (transmission = 92 % ± 5 %).

Peaks were assigned from the GC chromatogram for 1-alkenes assuming the 1-OH addition product is the major isomer due to alkyl radical stabilization (i.e. $f_{a1} > f_{a2}$). ~~For~~ In 2-methyl,2-butene, for similar reasons we assume 3-OH addition is formed in higher abundance than 2-OH addition for similar reasons (i.e. $f_{a3} > f_{a2}$).

The individual isomeric distributions derived from gas chromatography are listed in Table ~~5.~~45. ~~The transmission for all hydroxy nitrate isomers through the GC-CIMS/TD-LIF was measured to be 100 % ± 5 % except for 1-octene hydroxy nitrates (transmission= 92).~~

3.8 ~~Branching~~ Hydroxy nitrate branching ratios ~~to form hydroxy nitrates is independent of alkyl substituents of~~ depend on RO_2 substitution

There ~~has been significant controversy about whether the~~ is significant disagreement in the literature on the dependence of the yield of nitrates from $RO_2 + NO$ ~~is sensitive to~~ with the nature of R. A central question in this debate is whether the yields of nitrates from primary, secondary, and tertiary peroxy radicals are different (Orlando and Tyndall, 2012).

To determine the branching ratios of ~~beta~~ β hydroxy alkyl nitrates from specific ~~beta~~ β hydroxy peroxy radicals (α_1 and α_2), it is necessary to ~~normalize by~~ know the fraction of OH adding to each carbon (f_{a1} and f_{a2}). To estimate these fractions, we measured the isomer distribution of ~~beta~~ β hydroxy hydroperoxides formed from the reaction of RO_2 with HO_2. For these peroxy radicals, we assume that the yield of hydroperoxides from $RO_2 + HO_2$ reaction is unity (Raventos-Duran et al., 2007; Hasson et al., 2004; Spittler et al., 2000; Wallington and Japar, 1990a, b). ~~Thus~~We further assume that the CIMS sensitivity is the same for both isomers. With these assumptions, the ratio of the signal of the hydroxy hydroperoxides to hydroxy nitrate isomers provides an estimate of the difference in nitrate branching ~~ratio~~ ratios for the individual RO_2 isomers.

~~For propene, Cvetanovic (1976) (unpublished, as reported by Peeters et al. , 2007) measured the hydroxy hydroperoxide distribution , finding a 65/35 split between OH at vs. OH at . Peeters et al. (2007) presented a structure-activity relationship (SAR) for OH addition kinetics which predicts an 87/13 OH addition at vs. for 1-alkenes. For 1-butene, Peeters et al. (2007) determined a ratio of 85 : 15 using a mass spectrometer technique. Loison et al. (2010) used a similar technique, measuring the fraction of OH addition to each carbon using fragmentation patterns for the alkyl radical products. They measured a somewhat different ratio than the Peeters study: 70/30 split for OH addition at vs. for propene~~ The hydroxy hydroperoxide isomer distributions are listed in Table 45. It is difficult to ensure that the fate of peroxy radicals (RO_2) react only with HO_2 because the self reaction of HO_2 limits its abundance. There are, therefore, other reaction pathways that must be considered when interpretting the isomer distribution of hydroxy hydroperoxides, namely: $RO_2 + NO$; RO_2 H-shift isomerization, RO_2 + wall, and $RO_2 + RO_2$. $RO_2 + NO$ reactions should not disturb the ROOH isomeric distribution unless the $RO_2 + NO$ reaction rate constant differs between peroxy radicals. We did not detect products resulting from RO_2 H-shift isomerization, nor do we expect for these compounds to undergo H-shift isomerizations given the RO_2 lifetimes (estimated to be <0.2 s) in these experiments. For similar reasons, RO_2 + wall is not expected to be a large contribution, as the mixing time of our chamber (approximately 5 minutes) is two orders of magnitude slower than the RO_2 lifetime.

$RO_2 + RO_2$ chemistry will likely perturb the ROOH isomeric distribution due to the strong dependence of peroxy radical self-reaction rates on the alkyl substitution of R (Orlando and Tyndall, 2012 and references therein). We determined the isomer distribution sensitivity to $RO_2 + RO_2$ chemistry with propene by varying the ratio of HO_2 to RO_2 and measuring the subsequent hydroxy hydroperoxide isomer distribution. This was accomplished by increasing the ratio of hydrogen peroxide to initial alkene concentration (and thus the ratio of HO_2 to RO_2) at a given light flux ($j_{H2O2} \approx 2 \times 10^{-6} s^{-1}$). Conditions where the propene hydroperoxide isomer ratios reached a plateau was noted and ratios of the remaining hydroperoxides alkenes were measured at these conditions (see Fig. 48).

The inferred ratio of f_{a1} and ~~1-butene. Both studies were conducted in a flowtube at reduced pressure (2–5Torr,~~ f_{a2} is in reasonable agreement with the experimental findings of Cvetanovic (1976) (unpublished, as reported by Peeters et al., 2007~~; 0.8–3Torr,~~), Matsunaga and Ziemann (2009, 2010), Loison et al.~~,~~ (2010)~~. Krasnoperov~~ , and Peeters et al. (~~2011) measured branching ratios for OH+propene using labeled reactants to determine product distributions at 60–400 torr. They derived a ratio at odds with all previous findings, showing even distribution between products from OH addition at and . Feltham et~~ 2007) which all found OH addition favors formation of more stable alkyl radicals. In contrast, Krasnoperov et al. (~~2000) also measured site specific OH addition sites in sub-100temperatures in an argon matrix for a series of alkenes and included for completeness in Table 5.~~ 2011) suggested OH addition is equally distributed for propene.

~~We undertook a series of experiments to measure the hydroxy hydroperoxide isomer distribution using the same approach as described above for the hydroxy nitrates. We assume the same sensitivity for the two isomers in each system. Isomer distribution data is listed in Table 5. We derive a ratio between~~ Based on the f_{a1} and f_{a2} ~~that agrees well with the findings of Loison et al. (2010). We also find that the hydroxy hydroperoxide isomer distribution are identical (within error) to the hydroxy nitrate isomer distribution. This suggests thatthe specific~~ and hydroxy nitrate isomer distributions, we find that, for a given compound, the lesser substituted peroxy radical has a lower nitrate branching ratio ~~(α_1 or α_2) is determined primarily by the size of the Rradicaland is independent of whether the Ris primary, secondary, and tertiary . Additionally, the presence of the beta hydroxy group in relation to the peroxy radical does not appear to substantially alter the branching ratio toward formation of beta hydroxy nitrates as compared to those of n-alkanes of similar size.~~

4 ~~Atmospheric chemistry implications~~

~~In this study, we determined the hydroxy nitrate branching ratios, α, for a wide suite of alkenes. We recommend a revised parameterization for α based on the size of Rfor conditions of 298~~than the higher substituted peroxy radical. This result is consistent across all compounds studied except 1-hexene, where uncertainty stemming from losses in the GC is large. This finding is in contrast to studies of simple peroxy radicals where α for primary and ~~1: $\alpha = (0.042 \pm 0.008) \times N + (-0.11 \pm 0.04)$, where N =number of heavy atoms in the peroxy radical (excluding the peroxy radical moiety's two oxygen atoms), and listed errors are 2σ~~tertiary radicals have been found to be either equal to or less than α of secondary radicals (Arey et al., 2001; Espada et al., 2005; Cassanelli et al., 2007). Tyndall and Orlando (2012) cautioned that tertiary nitrates may have been underestimated in these studies due to losses of tertiary nitrates in gas chromatography.

A single $RO_2 + HO_2$ experiment (Experiment 37) was conducted with methylpropene to determine whether the assumption of unity yield of hydroxy hydroperoxides was valid. For methylpropene, the yield of acetone was found to be <5% as determined by GC-FID and proton transfer reaction MS. Only an upper bound for acetone production could be estimated due to significant signal interference by hydroxy hydroperoxides to the acetone signal in the GC-FID (see Appendix D).

~~The revision of branching ratios has a substantial impact on the predicted role of alkenes in the chemistry of~~

4 Atmospheric chemistry implications

Measurements of alkyl nitrates in the atmosphere have been used extensively to diagnose ozone and aerosol ~~. For ozone production,~~ formation (Rosen et al., 2004; Farmer et al., 2011; Perring et al., 2013). The development of methods described here for speciating these nitrates enables new opportunities to evaluate the role of ~~nitrate formation as a chain termination reaction~~ individual compounds towards oxidant formation in urban regions.

The rate of ozone production from an individual VOC precursor can be estimated ~~, assuming that the initial branching for the peroxy radical chemistry results in either formation of ozone or of organic nitrate . Typically, 2~~ from the rate of alkyl nitrate formation. For small molecules where alkoxy chemistry leads to fragmentation, approximately two ozone molecules are formed ~~per peroxy radical reacting with NOto form .~~ for each VOC-derived peroxy radical that reacts with NO. In addition, this chemistry yields reactive aldehydes that can lead to further oxidant production.

Neglecting entrainment or deposition and assuming an average alkyl nitrate branching ratio for the VOC mixture $\ll 1$, ~~one finds~~ yields the following relationship (Rosen et al., 2004; Farmer et al., 2011; Perring et al., 2013):

$$\frac{\Delta O_3}{\Delta \mathrm{ANs}} \approx \frac{P_{O_3}}{P_{\mathrm{ANs}}} \approx \frac{2(1-\alpha)}{\alpha} \approx \frac{2}{\alpha} \tag{3}$$

~~Examination of Eq. (3) suggests that increasing the nitrate branching ratios decreases the projected ozone production per VOC reacted. In Houston, where alkene oxidation is thought to significantly contribute to ozone formation, Rosen et al. (~~

In this study, the hydroxy nitrate branching ratios, α, are determined for a suite of alkenes. With this knowledge, we can estimate how much ozone (and, for terminal alkenes, how much formaldehyde) is produced for every alkyl nitrate formed. Recent research flights conducted over Houston as a part of the 2013 NASA SEAC4RS campaign provide an illustration of how measurements of hydroxy nitrates can be used to apportion the role of individual VOC precursors in oxidant formation.

Previous field studies in the Houston-Galveston airshed have yielded contradictory conclusions on the causes for the high ozone episodes experienced in the region. TexAQS I (2000) indicated the direct emission of ethene, propene, butadiene, and butenes were associated with rapid ozone production (Daum et al., 2003; Ryerson et al., 2003; Wert et al. 2003; Zhang et al. 2004)~~used this relationship to estimate the overall nitrate branching ratio (α). Using published branching ratios for alkenes (mostly O'Brien et al. , 1998), Rosen et al. (2004)could not reconcile the observed ozone , alkyl nitrates and alkene precursors. Using our experimentally derived hydroxy nitrate branching ratios for alkenes~~. Subsequently, however, data from TexAQS II (2005-6) indicated that primary or secondary emissions of formaldehyde and nitrous acid might contribute significantly to ozone production (Olaguer et al., 2009). Rappenglück et al. (2010) and Buzcu et al. (2011), for example, concluded that a quarter or more of the measured formaldehyde is directly emitted from vehicles. In contrast, Parrish et al., 2012, suggested that greater than 90% of the formaldehyde is produced via alkene oxidation. The disagreement on the source of formaldehyde has significant implications for ozone mitigation strategies (Olaguer et al., 2014).

Shown in Fig. 49 are Caltech CIMS measurements of hydroxy nitrates above Houston obtained during SEAC4RS flight of Sept. 18, 2013. During this flight, the NASA DC8 aircraft traversed Houston repeatedly sampling plumes of elevated ozone and formaldehyde. The measured hydroxy nitrates are highly correlated with elevated ozone and formaldehyde. Using equation 3, we find ~~a substantial increase in predicted alkyl nitrate production of 0.1969, compared to Rosen's estimate of 0.1516. The revised yields close approximately half the gap in observed vs. predicted nitrates. Tabulated data is shown in Table 6.~~ that the oxidation of small alkenes explains a large fraction of these enhancements. This finding is consistent with the earlier analysis of Rosen et al. (2004) and suggest that, a decade later, small alkenes remain a significant contributor to oxidant formation in Houston.

A much more complete investigation of the Houston airshed is underway making use of both the broad suite of measurements and large number of flights available from the SEAC4RS campaign (Thomas Ryerson, PI). Using the measurements of hydroxy nitrates, this study will offer regulators guidance in constructing effective ozone control strategies.

5 Conclusion

~~We measured~~ β hydroxy nitrate branching ratios for reactions of NO with RO_2 derived from the OH addition to linear and methyl-substituted alkenes ~~. We find these branching ratios~~ are reported. These observed branching ratios are found to be similar to those ~~found previously~~ previously observed for RO_2 derived from the OH oxidation of n-alkanes on a per-heavy-atom basis. Measurements of the hydroxy hydroperoxide isomer distributions from HO_2-dominated oxidation of propene, 1-butene, 2-methyl 2-butene, methylpropene, and 1-hexene suggest that there is ~~not~~ a significant difference in nitrate branching ratio~~between primary, secondary and tertiary Rradicals reacting with NO~~, and that these branching ratios increase with increasing substitution (primary <secondary <tertiary). We recommend the overall ~~beta~~ β hydroxy nitrate branching ratio from ~~beta~~ β hydroxy peroxy radicals ~~reacting with NO~~ produced from monoalkenes to be: ~~$\alpha = (0.042 \pm 0.008) \times N - (0.11 \pm 0.04)$,~~ $\alpha = (0.045 \pm 0.016) \times N - (0.11 \pm 0.05)$, where N is the total number of heavy atoms (for alkenes, N is the total number of ~~carbons~~ carbon atoms plus 1 for the OH that adds), and listed errors are 2σ. The branching ratio dependence on the number of heavy atoms is found to be the same (within error) to that derived for n-alkanes (Arey et al., 2001).

~~The atmospheric implications of our findings have a direct impact on our understanding of the the globally important formation of alkyl nitrates~~

Appendix A: Uncertainties

The following is a description of the uncertainties associated with each step in the analysis presented here:

1. The determination of CIMS sensitivities for β hydroxy nitrate compounds.
2. The relative determination of α. ~~Overall, projected and ozone concentrations will be lower where alkenes play an important role in~~
3. The absolute determination of α.
4. The hydroxy nitrate isomer distributions.
5. The hydroxy hydroperoxide isomer distributions.

A1 CIMS sensitivities derived from TD-LIF measurements

The uncertainties associated with determination of the CIMS sensitivity include: assumption that the conversion of β hydroxy nitrates is 100% in the TD-LIF; uncertainty in the split ratio of eluent flow between the CF_3O^- CIMS and TD-LIF; uncertainty in the absolute sensitivity to NO_2 in the TD-LIF; and integration errors associated with determining a baseline for trailing peaks in both the CF_3O^- CIMS and the TD-LIF chromatograms. Uncertainty in the conversion of hydroxy nitrates in the TD-LIF is discussed in Appendix A. Combined errors for the split flow ratio and absolute NO_2 determination are 10 %. Reproducibility of sensitivity from repeat chromatograms had errors than < 5 %, except for propene (< 15 %), which was signal-to-noise limited. It is possible that co-eluting compounds detectable in the TD-LIF but not the CF_3O^- CIMS would bias the CIMS sensitivity low. For hydroxy nitrates from d_6-propene and 1-octene, the CIMS measurement was assumed to have the same absolute sensitivity as hydroxy nitrates from propene and 1-hexene respectively. These were estimated to have an additional uncertainty of 3 %.

A2 Relative determination of α

Uncertainty in the estimate of the hydroxy nitrate branching ratios relative to $\alpha_{\mathrm{HN\_propene}}$ from Eq. (2) are determined by the relative uncertainties associated with the direct sampling CIMS measurement, the determination of CIMS sensitivities, the ratio of the OH reaction rate constants from the literature, uncertainties associated with determining the relative initial concentrations and the relative ratio of the secondary loss rates. Relative uncertainties in the k_{OH} rate constants were taken from Atkinson et al. (1983, 1986), and Aschmann and Atkinson (2008), and are reported to be < 6 %. The k_{OH} rate for d_6-propene was taken to be the same as k_{OH} for propene (Stuhl et al., 1998). PNNL spectral database IR cross sections were used to determine alkene gas concentrations, with an associated uncertainty of 2 %. For compounds with no published IR cross sections, the GC-FID signal was used to corroborate the pressure measurement. This contributes an additional 3 % uncertainty. Uncertainties in the CIMS quantification of hydroxy nitrates include background signal subtraction, signal to noise level, and equilibration-related time lags associated with lower volatility compounds. The combination of these uncertainties are estimated to be lower than 10 % for all compounds. Additional uncertainty in sensitivity for d_6-propene and 1-octene hydroxy nitrates was assumed to be 3 % because HNs derived from those compounds were not calibrated using the GC-TD-LIF technique.

A3 Absolute determination of α

As compared to the determination of α relative to $\alpha_{\mathrm{HN\_propene}}$, the absolute determination of α includes significant additional uncertainty associated with determining the total change in alkene concentration, the correction factors, F and F_{temp}, which account for secondary losses of hydroxy nitrates and the effect of increasing temperature from prolonged UV illumination of the chamber. The total change in alkene concentration includes uncertainty from the determination of total chamber volume (3%) and the GC-FID to quantify alkene loss (tabulated from repeat GC-FID measurements, and listed in Table 42). Secondary losses and temperature effects are tabulated in Table 42, and their uncertainties are taken to be half their total correction value. To determine an overall estimate for the branching ratio for a given compound, a reproducibility uncertainty (20%, estimated from the standard deviation of the propene experiments) was added to the average of multiple experiments.

A4 β hydroxy nitrate isomer distributions

Uncertainty estimates include uncertainty propagation from the CIMS sensitivity determination by TD-LIF for individual isomers, reproducibility of peak integration (± 2% for all compounds), discriminatory losses in the GC for 1-octene, and peak deconvolution for 2-methyl 2-butene HN isomers (an additional 7%). For all compounds listed, the GC transmission is found to be 100% ± 5%, except for 1-hexene $\mathrm{RONO_2}$, which had a transmission of 92% ±5%, which was assigned an additional error from this potentially discriminatory loss.

A5 β hydroxy hydroperoxide isomer distributions

Uncertainty in the isomer distribution contain contributions from the reproducibility in GC peak integrations, and discriminatory losses through the GC. Uncertainties in the GC peak integrations are <4% for all compounds, with an extra uncertainy of <5% assigned to 2-methyl 2-butene arising from peak deconvolution of an assumed Gaussian peak shape. For all compounds listed, the GC transmission is found to be 100% ± 5%, except for 1-hexene derived ROOH, which had a transmission of 50%. It is unclear for this compound whether the losses through the GC discriminated between the isomers, and therefore the uncertainties for this isomer distribution are large. Uncertainty from the impact of $\mathrm{RO_2 + RO_2}$ was determined to be negligible given that the distribution for propene hydroxy hydroperoxides plateaus at the experimental conditions in this work (Fig. 48). Further evidence for the negligible impact of $\mathrm{RO_2 + RO_2}$ is the lack of signals from dihydroxy and hydroxycarbonyl compounds in the CIMS observations. Experiments 25 and 26, conducted at higher ratios of alkene to hydrogen peroxide, had distinct dihydroxy and hydroxy carbonyl signals. The potential impact of $\mathrm{RO_2 + RO_2}$ was also estimated through kinetic box modeling in which the primary $\mathrm{RO_2}$ was allowed to react at a fast rate equivalent to peroxyacetyl radicals. The kinetic box modeling results, shown in Fig. 48, suggests that the impact of $\mathrm{RO_2 + RO_2}$ on the isomer distribution should be minimal over the experimental conditions. See Appendix C for a full description of the box model used. The uncertainty estimates do not take into account potential differences in the CIMS sensitivity for specific isomers as isomers were assumed to have the same sensitivity. For hydroxy nitrates isomers, aside from the 1-hexene HN, all isomers were determined to have very similar sensitivities.

Appendix B:

Conversion efficiency in the TD-LIF

The conversion efficiency of the ~~VOC budget.~~ TD-LIF instrument was evaluated with isopropyl nitrate. A known concentration of isopropyl nitrate was prepared in helium and sampled by the TD-LIF instrument. Oxygen addition upstream of the TD-LIF oven was increased until the $\mathrm{NO_2}$ signal downstream of the oven reached a plateau. This level was equal to the concentration of isopropyl nitrate (Fig. B1).

The conversion of $\mathrm{RONO_2}$ in the GC-CIMS/TD-LIF was also evaluated with isopropyl nitrate. A known amount of isopropyl nitrate was added into the chamber filled with air and sampled directly into the TD-LIF, bypassing the GC. A known volume of chamber air was then cryofocused onto the head of the GC column and analyzed in the same way described in Section 2. The signal from direct sampling and GC sampling agreed with the gravimetric determination to better than 10%.

The conversion of the TD-LIF was also evaluated with isoprene hydroxy nitrates (ISOPN). The ISOPN concentrations were measured directly with TD-LIF after addition of only ISOPN into the chamber. This measurement was, however, problematic due to long equilibration times (>3 hours) resulting from low sampling flow and small diameter tubing in the TD-LIF optimized for GC use. The sensitivity as determined by this measurement was 10-30% greater than the sensitivity determined through the GC for ISOPN compounds. Full equilibration of ISOPN in the direct sampling lines of the TD-LIF was never reached given the limited sampling time available for experiments. Direct sampling of the alkene-derived hydroxy nitrates discussed in this paper was not possible because authentic standards for these compounds were not available, and post-oxidation chamber air contains non-negligible levels of NO_2. Additionally, it has been observed that high concentrations of hydrogen peroxide perturbs the measurements of nitrates and NO_2 in the TD-LIF, particularly in the presence of NO. Using a GC to separate hydrogen peroxide, NO_2 and NO allowed measurements of hydroxy nitrate yields without these interferences.

SFig1.png

Figure B1. A graph showing the NO_2 recovery as a function of temperature. In red is shown the NO_2 recovery with addition of O_2 in the TD-LIF, and in black is NO_2 recovery without addition of O_2. Conversion of isopropyl nitrate is 100% in the TD-LIF.

Table C1. Box modeling reactions

Reactions	Rate constants
$H_2O_2 + h\nu \rightarrow OH + OH$	$2\times10^{-6}s^{-1}$
$H_2O_2 + OH \rightarrow HO_2 + H_2O$	1.8×10^{-12} $cm^3molec^{-1}s^{-1}$
$HO_2 + HO_2 \rightarrow H_2O_2$	$2.5\times10^{-12}cm^3molec^{-1}s^{-1}$
$OH + alkene \rightarrow 0.4primRO_2 + 0.6secRO_2$	2.63×10^{-11} $cm^3molec^{-1}s^{-1}$
$primRO_2 + primRO2 \rightarrow products$	$1.6\times10^{-11}cm^3molec^{-1}s^{-1}$
$primRO_2 + HO_2 \rightarrow primROOH$	$1\times10^{-11}cm^3molec^{-1}s^{-1}$
$secRO_2 + HO_2 \rightarrow secROOH$	$1\times10^{-11}cm^3molec^{-1}s^{-1}$

Appendix C:

Kinetic box modeling for hydroxy hydroperoxide isomer distribution

A kinetic box model of simplified chemistry in the hydroxy hydroperoxide yield experiments was used to understand the maximum potential impact of $RO_2 + RO_2$ reactions on the isomer distribution of hydroxy hydroperoxides. In the simplified chemistry only primary peroxy radicals self reactions are considered to occur with a fast reaction rate constant equivalent to the self reaction of peroxyacetyl radical (Atkinson et al., 2007). A rate constant for the RO_2 + HO_2 of 1×10^{-11} $cm^3molec^{-1}s^{-1}$ (slightly slower than the IUPAC recommended rate constant for hydroxy-ethene RO_2 + HO_2 (Atkinson et al., 2007)) is assumed. The products of RO_2 + RO_2 were assumed to be chain terminating to minimize subsequent production of HO_2. The model used the measured ratio of primary to secondary peroxides from propene of 0.39 : 0.61. Table C1 lists the considered reactions and accompanying rate constants. The box model was initialized with 2.5 ppmv H_2O_2 and propene concentrations varying from 1 ppbv to 150 ppbv. The box model was run for ten minutes, the approximate length of UV exposure for each hydroxy hydroperoxide isomer run.

The model runs suggests that at the ratio of initial alkene OH reactivity to hydrogen peroxide concentration used in this study, the hydroxy hydroperoxide isomer distribution are unaffected by RO_2 + RO_2 chemistry.

Appendix D:

Measurement of HO_x recycling for methylpropene

Acetone measurements in the GC-FID were used to infer the yield of HO_x recycling for $RO_2 + HO_2$ reactions occuring after OH and O_2 additions to methylpropene. These observations were were significantly impacted by methylpropene derived hydroxy hydroperoxides decomposing into acetone in the stainless steel sample loop. Similar decomposition of hydroxy hydroperoxides into carbonyls has been noted in other analytical instrumention, particularly from isoprene-derived hydroxy hydroperoxides decomposing into methacrolein and methyl vinyl ketone (Liu et al., 2013; Rivera et al., 2014). In order to measure the true acetone signal, a portion of the Teflon sample line was placed in a -50C isopropanol bath, a temperature that was sufficiently low to completely trap the hydroxy hydroperoxides while not retaining acetone. Blank GC runs with zero air were run until a negligible acetone signals were measured, at which point cold trapped samples of chamber air were analyzed. The result of removing hydroxy hydroperoxides while retaining acetone is shown in Figure 43, where the true acetone signal is shown to be low for Experiment 37.

The measurement of acetone was also confirmed with on-line measurements from the triple quadrupole CIMS instrument operated in positive mode with proton-transfer ionization. The predominant reagent ion in this mode is the protonated double cluster of water, $H_2O{\cdot}H_3O^+$. It was confirmed by measuring methylpropene-derived hydroxy hydroperoxides that this particular sampling and ionization method did not yield ions of protonated acetone from these hydroxy hydroperoxides in any significant yield.

SFig2.pdf

Figure D1. Cold trapping eliminates hydroxy hydroperoxides, removing an intereference to the measured acetone.

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Table 41. Experiment list.

Expt. #	H_2O_2 ppmv	NOv ppbv	VOC, ppbv			Absolute α	Relative α	ROOH yield	TD-LIF measurement
1	2	500	propene, 96	ISOPN, 50					x
2	2	500	propene, 93	ISOPN, 38					x
3	2	500	propene, 116	ISOPOOH, 38		x			
4	2	500	propene, 164	ISOPOOH, 50		x			
5		500	propene, 143	ISOPOOH, 44	CH_3ONO, 350	x			
6		500	propene, 156	ISOPOOH, 20	CH_3ONO, 370	x			
7	2.5	1200	propene, 262	1-butene, 183	1-pentene, 238	x			
8	2.5	1100	propene, 270	2-methyl 1-butene, 185	1-hexene, 180	x			
9	2.5	2300	propene, 235	1-hexene, 210		x			
10	2.5	1200	propene, 408	1-hexene, 390		x			
11	2.5	600	propene, 133	1,2 butanediol, 80		x			
12	1.0	600	propene, 162	1,2 butanediol, 490		x			
13	1.0	700	propene, 164	1,2 butanediol, 70		x			
14		600	propene, 122,	1,2 butanediol, 70	CH_3ONO, 60	x			
15	2	500	1-butene, 131	1-hexene, 105		x			x
16	2	500	1-butene, 15	cis-2-butene, 120		x			x
17	2	500	ethene, 1096	cis-2-butene, 115		x			x
18	2	500	2-methyl 2-butene, 107			x			x
19	2	500	methylpropene, 342			x			x
20	2.6		propene, 9					x	
21	2.6		propene, 8					x	
22	2.6		propene, 5					x	
23	10.4		propene, 7					x	
24	2		propene, 21					x	
25	2		propene, 36	1-butene, 17	1-hexene, 33			x	
26	2		propene, 30	butadiene, 14	2-methyl 2-butene, 20			x	
27	2.7		1-hexene, 5					x	
28	2.7		2-methyl 2-butene, 4					x	
29	2.8		methylpropene, 4					x	
30	2.8		1-butene, 7					x	
31	2	1000	d_6-propene, 324	1-butene, 256			x		
32	2	1000	d_6-propene, 280	propene, 334.5	1-butene, 102		x		
33	2	1140	ethene, 963	propene, 426	methylpropene, 261		x		
			2-methyl 2-butene, 242	1-hexene, 254	1-octene, 326				
34	0.2	1930	ethene, 2983	propene, 608	methylpropene, 309		x		
			2-methyl 2-butene, 339	1-hexene, 263	1-octene, 314				
35	0.2	950	propene, 1418	1-butene, 85	methacrolein, 902		x		
			2,3 dimethyl,2-butene, 1096						
36	0.2	950	propene, 1380	methyl vinyl ketone, 1258	cis-2-butene, 674		x		
			2,3-dimethyl 2-butene, 732						
37	20		methylpropene, 181					x	

Table 42. Sensitivities for hydroxy nitrates in $\mathrm{CF_3O^-}$ CIMS derived from GC-CIMS/TD-LIF technique.

Hydroxy Nitrates Derived From:	Measured CIMS $\mathrm{CF_3O^-}$ Sensitivity $(\mathrm{normcts\,pptv^{-1}}), 10^4$
Ethene, 1-OH, 2-$\mathrm{ONO_2}$	$\mathbf{3.5 \pm 0.4}$
Propene 1-OH, 2-$\mathrm{ONO_2}$	5.0 ± 1.2
Propene 2-OH, 1-$\mathrm{ONO_2}$	5.0 ± 1.4
Propene, both	$\mathbf{5.0 \pm 1.0}$
1-Butene 1-OH, 2-$\mathrm{ONO_2}$	3.3 ± 0.5
1-Butene 2-OH, 1-$\mathrm{ONO_2}$	2.9 ± 0.4
1-Butene, both	$\mathbf{3.1 \pm 0.4}$
cis-2-Butene, first diastereomer	2.8 ± 0.4
cis-2-Butene, second diastereomer	2.9 ± 0.4
cis-2-Butene, both	$\mathbf{2.9 \pm 0.4}$
Methylpropene 1-OH, 2-$\mathrm{ONO_2}$	3.9 ± 0.4
Methylpropene 2-OH, 1-$\mathrm{ONO_2}$	3.7 ± 0.8
Methylpropene, both	$\mathbf{3.8 \pm 0.5}$
2-Methyl,2-Butene 2-OH, 3-$\mathrm{ONO_2}$	3.8 ± 0.4
2-Methyl,2-Butene 3-OH, 2-$\mathrm{ONO_2}$	3.8 ± 0.5
2-Methyl,2-Butene, both	$\mathbf{3.8 \pm 0.4}$
1-Hexene, 1-OH, 2-$\mathrm{ONO_2}$	2.6 ± 0.3
1-Hexene, 2-OH, 1-$\mathrm{ONO_2}$	2.0 ± 0.4
1-Hexene, both	$\mathbf{2.4 \pm 0.3}$

Absolute sensitivities for all isomers were determined by summing all peaks in both the CIMS and TD-LIF, and deriving a sensitivity from the total. Uncertainties (1σ) include the 10 % uncertainty from the split ratio and absolute $\mathrm{NO_2}$ determination by the TD-LIF. The measured 1-hexene HN sensitivities are lower than other HNs measured in this study. This may reflect precision errors for this one compound, and thus lead to a high biasing in the HN branching of 1-hexene and 1-octene.

Table 43. Absolute Hydroxy Nitrate (HN) Yields from Alkenes at 293K and 993hPa.

Alkene	Δ Alkene ppbv/%	HN, ppbv	$k^1_{\mathrm{OH,HN}}$ ($\times 10^{-11}$) (cm^3 molec^{-1} s^{-1})	k^2_{w}($\times 10^{-6}$) (s^{-1})	F^3	F^4_{temp}	$Y_{\beta\mathrm{HN}}$ (%)	f^5_{a}	α (%)
ethene	221/21(±2)	2.6 ± 0.5	0.3	3.8	1.06	1.02	1.3±0.2	1	1.3±0.2
overall ethene									**1.3**±0.5
propene	38/32(±3)	1.6 ± 0.4	0.6	1.6	1.05	1.01	4.4±1	0.97	4.6±1
propene	60/37(±4)	2.4 ± 0.6	0.6	1.6	1.07	1.01	4.3±1	0.97	4.4±1
propene	104/39(±4)	4 ± 0.8	0.6	1.6	1.07	1.05	4.3±1	0.97	4.5±1
propene	83/31(±2)	3.7 ± 0.8	0.6	1.6	1.05	1.05	4.7±1	0.97	4.8±1
propene	71/18(±2)	2.9 ± 0.6	0.6	1.6	1.03	1.04	4.4±1	0.97	4.1±1
propene	68 /33(±2)	2.4 ± 0.5	0.6	1.6	1.09	1.04	4.0±1	0.97	4.1±1
propene	34 /21(±3)	1.2 ± 0.3	0.6	1.6	1.03	1.03	3.7±1	0.97	3.9±1
propene	59 /36(±4)	2.1 ± 0.5	0.6	1.6	1.05	1.06	4.0±1	0.97	4.1±1
propene	42 /34(±4)	1.5 ± 0.4	0.6	1.6	1.05	1.01	3.8±1	0.97	3.9±1
overall propene									**4.1**±2
1-butene	71/55(±4)	6.8 ± 1.2	0.7	3.7	1.1	1.06	11±2	0.92	12±2
1-butene	78/43(±3)	7.6 ± 1.3	0.7	3.7	1.09	1.06	12±2	0.92	13±2
overall 1-butene									**12**±5
cis-2-butene	85/74(±5)	8.4 ± 1.3	0.6	4	1.11	1.06	12±2	0.97	12±2
overall cis-2-butene									**12**±4
methylpropene	166/49(±3)	13.7 ± 1.9	0.5	6.5	1.05	1.05	9±1	0.97	9±1
overall methylpropene									**9**±3
2-methyl 1-butene	114/60(±4)	15.5 ± 3.9	0.8	2	1.08	1.05	15±4	0.95	16±4
overall 2-methyl 1-butene									**16**±7
2-methyl 2-butene	66/64(±4)	5.3 ± 0.8	0.8	8.3	1.07	1.04	9±2	0.97	9±2
overall 2-methyl 2-butene									**9**±4
1-pentene	108/44(±3)	12 ± 3	0.85	6.7	1.12	1.05	13±3	0.87	15±3
overall 1-pentene									**15**±6
1-hexene	62/59(±6)	9.2 ± 1.5	1	10	1.2	1.06	19±3	0.86	22±4
1-hexene	78/43(±4)	11.8 ± 1.9	1	10	1.13	1.07	18±3	0.86	21±4
1-hexene	91/23(±2)	14.6 ± 2.4	1	10	1.06	1.06	18±3	0.86	21±4
overall 1-hexene									**21**±8

[1] Rate constants are from Treves and Ruddich, 2003 or estimated based on Treves and Ruddich, 2003.

[2] Wall loss rate constants are calculated from post experiment HN signal decay.

[3] Correction factor F accounts for loss of hydroxy nitrates due to wall loss and reaction with OH. This factor was calculated using a modified equation for F described by Atkinson et al., 1982, where $k_7 = k_{\mathrm{OH,alkene}} \times [\mathrm{OH}]_{\mathrm{average}}$, and $k_{10} = k_{\mathrm{OH,HN}} \times [\mathrm{OH}]_{\mathrm{average}} + k_{\mathrm{w}}$, where $[\mathrm{OH}]_{\mathrm{average}}$ is calculated using alkene decay.

[4] Correction factor F_{temp} accounts for the change in α in response to temperature variation during the experiment. This factor was estimated using the temperature dependence of α reported by Arey et al. (2001).

[5] See text for more details on estimates for normalization for the fraction of OH + alkene that proceeds via OH addition, f_{a}.

Table 44. ~~Branching Ratios~~ β HN sensitivities, OH rates, f_a, relative $Y_{\beta\mathrm{HN}}$, $\alpha_{alkene}/\alpha_{propene}$ and branching ratios to ~~Form Hydroxy Nitrates~~ form β hydroxy nitrates (HN) at 293K and 993hPa.

alkene	Relative CIMS sensitivity	Relative $k_{\mathrm{OH,alkene}}$	Relative $Y_{\beta\mathrm{HN}}$	OH addition fraction, f_a[d]	$\alpha_{alkene}/\alpha_{propene}$	α (%)	previously reported $Y_{\mathrm{total}\ N}$ ([a] = only $Y_{\beta\mathrm{HN}}$)
ethene	0.7±0.08	0.323±0.04	0.51±0.1	1	0.49±0.1	2.2±0.6	0.86 ± 0.03[a]
ethene	0.7±0.08	0.323±0.04	0.51±0.08	1	0.49±0.08	2.2±0.5	
propene	1±0.2	1±0	1±0.2	0.97	1±0.2	4.4±1	1.5 ± 0.1[a]
d_6-propene	1±0.2[c]	1±0.07	1.5±0.3	1	1.5±0.3	6.6±2	
1-butene	0.62±0.08	1.19±0.05	2.6±0.4	0.92	2.7±0.4	12±3	2.5 ± 0.2[a]
1-butene	0.62±0.08	1.19±0.05	2.6±0.4	0.92	2.8±0.4	12±3	
1-butene	0.62±0.08	1.19±0.05	2.6±0.4	0.92	2.8±0.4	12±3	
cis-2-butene	0.58±0.08	2.13±0.02	2.5±0.4	0.97	2.5±0.4	11±2	3.4 ± 0.5[a]
cis-2-butene	0.58±0.08	2.13±0.02	2.3±0.3	0.97	2.3±0.3	10±2	
methylpropene	0.76±0.1	1.95±0.05	2.4±0.4	0.97	2.4±0.4	10±2	6 ± 2.1[b]
methylpropene	0.76±0.1	1.95±0.05	2.4±0.5	0.97	2.4±0.5	11±3	
methylpropene	0.76±0.1	1.95±0.05	2.4±0.4	0.97	2.4±0.4	11±2	
methylpropene	0.76±0.1	1.95±0.05	2.4±0.4	0.97	2.4±0.4	11±2	
2-methyl 2-butene	0.76±0.08	3.3±0.04	2.5±0.4	0.97	2.5±0.4	11±2	9 ± 3.1[b]
2-methyl 2-butene	0.76±0.08	3.3±0.04	2.4±0.3	0.97	2.4±0.3	10±2	
1-hexene	0.48±0.06	1.4±0.03	4.7±0.8	0.85	5.4±0.9	24±5	5.5 ± 1.0[a]
1-hexene	0.48±0.06	1.4±0.03	4.6±0.7	0.85	5.2±0.8	23±5	
1-octene	0.48±0.06[c]	1.62±0.05	5.5±0.9	0.78	7±1	30±7	13 ± 4.5[b]
1-octene	0.48±0.06[c]	1.62±0.05	4.8±0.7	0.78	6±1	29±6	

[a] O'Brien et al.,1998, only hydroxy nitrate yield

[b] Tuazon et al. (1998)

[c] Estimated values. For d_6-propene hydroxy nitrates, the sensitivity is assumed to be the same as propene hydroxy nitrates. For 1-octene hydroxy nitrates, the sensitivity was assumed to be the same as 1-hexene hydroxy nitrates.

[d] See the text for how the fraction of reactivity with OH occuring by addition (f_a) is estimated.

Table 45. Isomer distribution for hydroxy nitrates and hydroxy hydroperoxides formed from OH addition to alkenes.

alkene	product	X=ONO$_2$ % isomer distribution	X=OOH % isomer distribution	$\alpha_1 : \alpha_2$	previously reported % distribution	type of reported distribution
propene	1-X, 2-OH : 2-X, 1-OH	$31 \pm 7 : 69 \pm 7$	$40 \pm 3 : 60 \pm 3$	$1 : 1.5^{+0.3}_{-0.2}$	40 : 60[a]	ONO$_2$ isomers
					28 : 72[b]	OH branching
					35 : 65[c]	OH branching
					50 : 50[e]	OH branching
					50 : 50[f]	OH branching
1-butene	1-X, 2-OH : 2-X, 1-OH	$27 \pm 7 : 73 \pm 7$	$35 \pm 3 : 65 \pm 3$	$1 : 1.5^{+0.3}_{-0.3}$	44 : 56[a]	RONO$_2$ isomer
					29 : 71[b]	OH branching
					15 : 85[d]	OH branching
cis 2-butene	2-X, 3-OH [(R,S) and (S,R)] : 2-X, 3-OH [(S,S) and (R,R)]	$50 \pm 6 : 50 \pm 6$				
2-methylpropene	1-X, 2-OH : 2-X, 1-OH	$11 \pm 3 : 89 \pm 3$	$21 \pm 2 : 79 \pm 2$	$1 : 2.2^{+0.9}_{-0.6}$	15 : 85[d]	OH branching
2-methyl 2-butene	2-X, 3-OH, 3-methyl : 3-X, 2-OH, 3-methyl	$18 \pm 10 : 82 \pm 10$	$31 \pm 6 : 69 \pm 6$	$1 : 2.0^{+2.4}_{-0.7}$	44 : 66[d]	OH branching
1-hexene	1-X, 2-OH : 2-X, 1-OH	$28 \pm 7 : 72 \pm 7$	$30^{+23}_{-14} : 70^{+14}_{-23}$	$1 : 1.1^{+0.9}_{-0.8}$	42 : 58[a]	RONO$_2$ isomer
1-octene	1-X, 2-OH : 2-X, 1-OH	$14 \pm 15 : 86 \pm 15$				
1-alkene (C_{14} to C_{17})	1-X, 2-OH : 2-X, 1-OH				30 : 70[g]	RONO$_2$ isomer
2-methyl 1-alkene (C_{15})	1-X, 2-OH : 2-X, 1-OH				10 : 90[g]	RONO$_2$ isomer

[a] O'Brien et al. (1998) [b] Loison et al.(2010) [c] Cvetanovic (1976) [d] Peeters et al.(2007) [e] Feltham et al., (2000) [f] Krasnoperov et al. (2011) [g] Matsunaga and Ziemann et al. (2009; 2010) .

Table 46. Using revised alkyl nitrate yields to ~~interpret~~ re-interpret 2000 TexAQ data (Rosen et al., 2004).

Compound	ppbv	P_{O_3}, ppbv h^{-1}	% P_{O_3}	Yield	$P_{\Sigma AN}$, ppbv h^{-1}	% $P_{\text{sum(ANs)}}$
butanes	6.68	0.31	4.9	0.079	0.0092	4.69
pentanes	3.56	0.26	4.2	0.101	0.0103	5.27
ethene	4.81	0.58	9.2	0.023	0.0068	3.46
propene	1.27	0.46	7.3	0.051	0.0123	6.27
isoprene	0.20	0.25	4.0	0.135	0.0196	10.03
other alkanes	22.60	0.51	8.2	0.044	0.0268	13.67
other $C_4 - C_{10}$ alkenes	1.74	1.22	19.5	0.109	0.0754	38.52
aromatics	2.71	0.55	8.7	0.100	0.0303	15.50
aldehydes	7.41	1.42	22.7	0	0	0
CO, CH_4	2000	0.54	8.6	0	0	0
other	6.19	0.17	2.7	0.026	0.0051	2.59
total		6.27	100	0.045	0.1957	100

Yields have been updated using values from this study. Ethene, propene, 1-butene, cis-2-butene, methylpropene, 1-pentene, 2-methyl 1-butene, 1-hexene, 2-methyl 2-butene use the yields determined here. The following values have been changed to reflect the estimated value based on this work: 1,3-butadiene: 0.10, trans-2-butene, 0.10; 3-methyl 1-butene, 0.13; cis-2-pentene, 0.14, isoprene: 0.12 methacrolein: 0.033, methyl vinyl ketone: 0.040. Alkane values have been re-adjusted to better reflect the parameterization in Arey et al., 2001: i-butane from 0.255 to 0.077; i-pentane from 0.35 to 0.10; nonane from 0.05 to 0.17.

~~Reaction Pathways of Alkenes with OH: OH oxidation with alkenes follows two pathways: OH addition (f_n and f_{n+1}) and H-abstraction (f_b, where $f_b = \Sigma(f_{b1} \ldots f_{bn})$). The sum of ($f_a + f_b$) equals 1. Subscripts indicate the carbon number at which either OH addition or abstraction occurs. For alkenes studied in this work at room temperature, the sum of f_{an} and f_{an+1} is much greater than f_b. See text for further discussion of estimations for f_b.~~

fig1.jpg

Figure 41. ~~Shown is an example~~ Reaction pathways of alkenes with OH. OH oxidation ~~experiment in which 6~~ with alkenes ~~are added to~~ follows two pathways: OH addition (f_n and f_{n+1}) and H-abstraction (f_{ab}, where $f_{\mathrm{ab}} = \sum_{n=1}^{l} f_{\mathrm{ab}n}$). f_{a} + f_{ab}) = 1. Subscripts indicate the ~~chamber~~carbon number at which either OH addition or abstraction occurs. For alkenes studied in this work at room temperature, the sum of $f_{\mathrm{a}n}$ and ~~their~~ $f_{\mathrm{a}n+1}$ is much greater than f_{ab}. See text for further discussion of estimations for f_{ab}.

Fig2_rev.pdf

Figure 42. β hydroxy nitrate products ~~are monitored simultaneously~~produced from six alkenes during Exp. 19. The top panel shows the ratio of CIMS hydroxy nitrate (HN) signals ratioed to propene HN (206 m/z) for: ethene HN (192 m/z, blue), methylpropene HN (220 m/z, red), 2-methyl,2-butene HN (234 m/z, teal), 1-hexene HN (248 m/z, purple), and 1-octene HN (276 m/z, gold). The bottom panel shows the absolute signal for propene HN (206 m/z). The lights were turned on at time = 0, and turned off at 7 min (vertical ~~dashed~~ line), at which point the oxidation stopped. For all compounds other than hydroxy nitrates from 1-octene, a ratio is plotted as a dashed line using averaged data from three minutes after lights until the measurements stopped. For hydroxy nitrates from 1-octene, data after 10 min is averaged. The time lag for hydroxy nitrates from 1-octene arises from wall and sample line equilibration. This suggests that the measured yield is ~~likely~~ a lower limit.

Fig3_Rev.png

The ~~hydroxy~~ assigned chemical structures are shown for each alkyl nitrate ~~branching ratios after OH and addition plotted against the number of heavy atoms (not including the peroxy radical moiety) derived from a subset of alkenes in this study~~peak.~~Data is taken from Table 3 and normalized by f_{a} to account for abstraction chemistry (see text for more details). An OLS fit is shown in the dotted red line, with a slope of 0.042 ± 0.008 and an intercept of −0.11 ± 0.04.~~

The ~~hydroxy~~ assigned chemical structures are shown for each alkyl nitrate ~~branching ratios after OH and addition plotted against the number of heavy atoms (not including the peroxy radical moiety) derived from a subset of alkenes in this study~~peak.~~Data is taken from Table 3 and normalized by f_{a} to account for abstraction chemistry (see text for more details). An OLS fit is shown in the dotted red line, with a slope of 0.042 ± 0.008 and an intercept of −0.11 ± 0.04.~~

Figure 43. ~~An example~~ GC-CIMS/TD-LIF chromatogram ~~is shown~~following Exp. ~~Absolute amounts of~~ 15. The signals due to individual hydroxy ~~nitrate~~ nitrates are ~~measured~~ determined by integrating the alkyl nitrate peaks (black line, elevated baseline) which co-elute with the individual hydroxy nitrates observed by CIMS, e.g. hydroxy nitrates from 1-butene at 220 m/z (blue) and from 1-hexene at 248 m/z. Absolute CIMS sensitivities are determined by integrating individual peaks for CIMS signal and TD-LIF signal and dividing.

The ~~hydroxy~~ assigned chemical structures are shown for each alkyl nitrate ~~branching ratios after OH and addition plotted against the number of heavy atoms (not including the peroxy radical moiety) derived from a subset of alkenes in this study~~peak.~~Data is taken from Table 3 and normalized by f_{a} to account for abstraction chemistry (see text for more details). An OLS fit is shown in the dotted red line, with a slope of 0.042 ± 0.008 and an intercept of −0.11 ± 0.04.~~

Fig5_rev.pdf

Figure 44. The isomer-averaged branching ratios, α, derived in this study (~~black circles~~blue boxes, data from Table ~~4~~**??**), compared to ~~similar carbon numbered n-alkanes~~ previously published nitrate branching ratios (Arey et al., 2001 ~~;~~ with pink exes~~) and previously published nitrate branching ratios (~~; O'Brien et al., 1998 ~~;~~ with green stars). Alkene nitrate yields from O'Brien et al., 1998 have been normalized by f_{a} to account for H-abstraction channel in the same fashion as this study. The ~~OLS~~ error weighted fit derived from Fig. ~~4~~ 45 is shown for hydroxy nitrate branching ratios (~~red~~ black dotted line) from all measured alkenes yields a slope of ~~0.042 ± 0.008~~ 0.045 ± 0.016 and intercept of ~~-0.11 ± 0.04~~ -0.11 ± 0.05 (errors are 2σ). This fit agrees well with the relationship derived by Arey et al., 2001, who calculated a slope of 0.0381 ± 0.0016 and an intercept of -0.073 ± 0.009 for ~~alkanes~~n-alkanes.

Fig6_rev.png

Figure 45. Alkoxy H-shift isomerization leading to dihydroxy nitrate formation for 1-hexene.

Fig7_rev.pdf

Figure 46. ~~An example~~ A chromatographic separation of hydroxy nitrates formed from a set of alkenes ~~.~~ in Experiment 19. 192 $m/z=$ ethene hydroxy nitrate, 206 $m/z=$ propene hydroxy nitrate; 220 $m/z=$ methylpropene hydroxy nitrate; 234 $m/z=$ 2-methyl 2-butene hydroxy nitrate; 248 $m/z=$ 1-hexene hydroxy nitrate; 276 $m/z=$ 1-octene hydroxy nitrate. Isomer distributions were determined based on integrating peak areas from chromatograms. The later eluting peaks are prone to tailing and co-elution. In such cases, Gaussian peaks shapes were ~~fit~~ used to deconvolute co-eluting isomers and the trailing tail ~~residual~~ was assigned to the later eluting peak.~~This approach is consistent with the fact that the wider and larger peak elutes later in all cases for these hydroxy nitrates.~~

Fig8_rev.pdf

Figure 47. The measured isomer distribution of propene hydroxy hydroperoxides (blue boxes) as a function of the initial alkene OH reactivity and the initial hydrogen peroxide concentration. The red line represents the alkene OH reactivity regime over which hydroxy hydroperoxide isomer distributions were reported for all alkenes other than propene. The dashed black line represents a kinetic box model simulation designed to study the maximum impact $\mathrm{RO_2 + RO_2}$ chemistry might have on the isomer distributions. See Appendix B for further details on the kinetic model.

Fig9_rev.pdf

Figure 48. Atmospheric hydroxy nitrate, O_3 and formaldehyde data measured in the Houston plume from the 2013 SEAC4RS campaign. The lower right panel shows how each hydroxy nitrate contributes to the total hydroxy nitrate measured by the Caltech CIMS for the data taken from a flight over Houston on September 18, 2013. As the plane crosses into the Houston plume, hydroxy nitrates derived from anthropogenic emissions are enhanced. The upper right panel shows formaldehyde (black, left axis) and ozone (red, right axis) is strongly correlated with anthropogenically derived hydroxy ntirates. Additionally, the lower bound estimates for the formaldehyde directly attributable to oxidation of each alkene in-plume using the branching ratios derived in this study are shown in colors. For ethene, the contribution is adjusted to produce two formaldehyde molecules after alkoxy decomposition, and uses a decomposition yield of 0.8 to account for glycolaldehyde formation from reaction of the alkoxy radical reaction with O_2. For isoprene hydroxy nitrate, a branching ratio estimate of 0.12 was used (Paulot et al., 2009). It was assumed that the sum of methyl vinyl ketone hydroxy nitrate (MVKN) and methacrolein hydroxy nitrate (MACRN) are exclusively derived from isoprene hydroxy nitrates with a yield of 1 formaldehyde per each isoprene HN oxidized to form a MVKN or MACRN molecule (Lee et al., 2014), and, therefore, a branching ratio estimate of 0.11 was used. Ozone observations were provided courtesy of Ryerson, Pollack and Peischl at NOAA ESRL. Formaldehyde observations provided courtesy of Hanisco and Wolfe at NASA. The left panel graphs the flight tracks for this section of the flight colored by the lower bound estimate of formaldehyde formed from oxidation of alkenes. Satellite image courtesy of NASA's AERONET.