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Atmospheric Chemistry and Physics
Discussions

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

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We thank the reviewer for these comments.

‘’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.”

‘’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 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}.

‘’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

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.

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

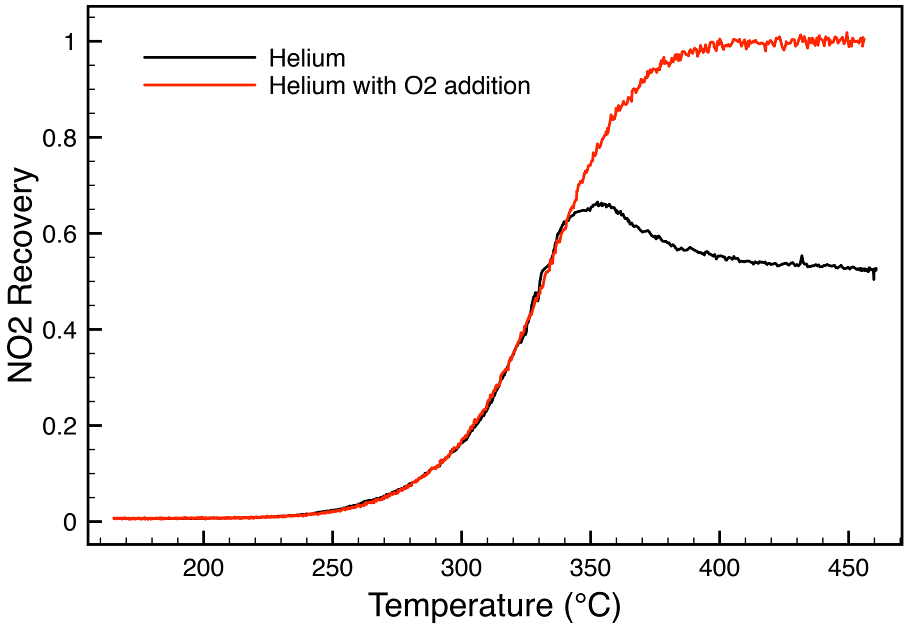
NO2 Recovery
0
0.2
0.4
0.6
0.8
1
Helium
Helium with O2 addition
200
250
300
350
400
450
Temperature (°C)

Fig. 1.