Response to reviews

Reviewer comments are in **bold**. Author responses are in plain text. Modifications to the manuscript are in *italics*. Line numbers in the responses correspond to those in the ACPD paper.

Reviewer #1

The paper presents interesting results concerning clean-air isoprene oxidation. Experiments were conducted in conditions where the dominant fate of organic peroxyl radicals (RO_2) is reaction with HO_2. The authors have observed formation of small but significant yields of methacrolein (MACR) and methyl vinyl ketone (MVK), and present a convincing argument that these products result from radical recycling chemistry. Specifically, an OH yield of 7 % is derived for the reaction (R1) of HO_2 with the various isomeric RO_2 derived from isoprene (ISOPOO).

ISOPOO + HO_2 →ISOPOOH + O_2 (R1a)

→OH + ISOPO + O_2 (R1b)

Two of the ISOPO products are known to decompose to form MVK and MACR, with concurrent production of HO_2, hence detection of MVK or MACR from isoprene in such (NO_x free) conditions may be used as evidence for OH production in (R1). In reporting MVK, MACR, OH and overall HO_x yields following R1, the paper contains data and implications of considerable value to the atmospheric science community. However, some corrections and clarifications are required prior to publication in ACP, in particular regarding the distribution of ISOPOO available to react with HO_2, and the quoted uncertainties in the reported MVK, MACR and HO_x yields.

We thank the reviewer for the detailed and helpful comments focused on improving the manuscript. Responses to the individual comments are given below.

(1) In the introduction to HO_2+ RO_2 chemistry (page 3 line 52) it is stated that OH productions "has been demonstrated in the laboratory only for carbonyl-bearing RO_2". This is not quite the case. The only direct detection of OH was in the Dillon & Crowley study, and there only for carbonyl RO2. However, Jenkin and co-workers have shown that OH is produced in reactions of HO_2 with two RO_2 without carbonyl substitution, $HOCH_2O_2$ (Jenkin et al. 2007) and $CH_3OCH_2O_2$ (Jenkin et al. 2008).

We thank the reviewer for this input. The sentence is revised as follows:

"This type of reaction has been demonstrated in the laboratory for some RO_2 radicals (Sulbaek Andersen et al., 2003; Hasson et al., 2004; Jenkin et al., 2007, 2008; Dillon and Crowley, 2008). Theoretical studies suggest that this reaction is favored for peroxyl radicals having the forms RCHXOO and RCHXCH$_2$OO that can pass through a hydrotetroxide intermediate, where X is an electronegative atom(Hasson et al., 2005)."

(2) The authors have taken care to design experiments where the production of MVK & MACR can be confidently attributed to ISOPOO + HO_2 (R1). A number of tests were carried-out to quantify / eliminate alternative chemistry leading to MVK & MACR.

Nonetheless, I feel there are several points in the manuscript where further discussion and quantification of possible errors in MVK & MACR yields is necessary:

In sections 2, 3.1 & 3.6 a low temperature trap is mentioned. This is used to remove interference from low-volatility products ISOPOOH and IEPOX in the detection of MVK and MACR. Sensitivities to isoprene, MEK & MACR were unchanged, indicating that these compounds were not trapped. Can you quantify how efficient the trap was at removing ISOPOOH and IEPOX? This is crucial for assessing how much MEK and MACR were really derived from R1.

The signal intensities of the $C_4H_5O^+$ and $C_4H_6NO_2^+$ ions in the HO_2-dominant experiments dropped significantly from 0 to -30 ℃, with no further observable change from -30 to -40 ℃. This observation suggests that the interference compounds, possibly ISOPOOH, were fully removed. Fig. 6 shows these results, with associated discussion in the manuscript (Page 33339 Line 16-21). For further clarification, the revised text reads:

"The signal intensities were independent of temperature from -30 to -40 ℃, meaning that the interference products were fully removed from the gas phase at the trap temperature below -30 ℃ and hence the $C_4H_5O^+$ and $C_4H_6NO_2^+$ ions at -40 ℃ represented the instrument response to MACR and MVK."

(3) On page 33333 yields of MEK and MACR are derived via equation 2. This section is confusing, as rate coefficients k_1 & k_2 here do not correspond to the reactions R1 and R2 from the text, but instead to reactions of OH with isoprene and MVK. Please write out these reactions explicitly, and re-number them so that k_1 corresponds to R1, k_2 to R2 etc. In the text below I use k_1 to refer to the rate of ISOPOO + HO_2 (R1 in the manuscript text).

We thank the reviewer for pointing out this confusion. The revised text is clarified. Rate constants k_1 and k_2 are changed to $k_{C_5H_8+OH}$ and k_{MVK+OH}, respectively.

(4) Also in equation 2, a wall-loss rate of 0 s^{-1} is reported. Could you be more precise regarding this parameter? No mention is made of wall-loss rates for radicals OH, HO_2 or ISOPOO. Are these important, or taken into account in this analysis? I note that for HO_2 levels of 540 ppt, and using $k_1 = 1.7\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} a first-order rate for (R1) of $k_1[HO_2] \approx 0.2$ s^{-1} may be derived, so even small losses of ISOPOO elsewhere (eg. near 0 s^{-1} to the wall or by photolysis) may be important. That the lifetime of ISOPOO is of the order of a few seconds is important – see the comments on Table 3 and on Figure 1 below.

In Equations 1 and 2, k_{wall} refers to the steady-state wall loss rate of MVK (Page 33333 Line 19). It was measured as zero by a separately conducted wall-loss experiment described in the supplementary material.

We do not think that the wall-loss rates of OH radicals are important in the analysis. The steady-state OH concentration used in Equations 1 and 2 was determined experimentally based on the mass balance of isoprene, as shown in Equation 3.

Equations 1 and 2 define the measured yields of MVK and MACR from the reaction series of isoprene and OH. As emphasized by the reviewer, the measured yields could change significantly for different experimental conditions depending on the fate of ISOPOO, among other factors. Uncounted-for wall loss of HO_2 and ISOPOO and photolysis of ISOPOO can potentially influence the yields of MVK and MACR attributed to the HO_2 pathway (i.e., the final yields reported in this work.)

In the case of significant wall loss of HO_2 radicals, the HO_2 level in the chamber could be lower than our estimate (540 ppt for Experiment #1), which does not account for wall loss. The implication could be that the contribution of the HO_2 pathway to ISOPOO fate could potentially be overestimated, as stated by the reviewer. McMurry and Grosjean (1985) provided a formulation to estimate the lifetime of gas-phase species in a chamber against wall collisions. For the experimental conditions of the present study, the estimate is on order of 10^3 s. The lifetime of HO_2 against gas-phase reaction was 10 s in Experiment #1 based on MCM simulation, suggesting that wall collisions were at most of minor importance for the fate of HO_2. Moreover, the conclusion that the HO_2 pathway was the dominant fate of ISOPOO in Experiment #1 does not rely solely on the model simulations. It was also verified experimentally by observing the effects of doubling and halving the H_2O_2 concentration (Page 33336 Line 9-26).

We agree with the reviewer that wall loss and photolysis could be competing reaction pathways of ISOPOO. They are, however, probably less important ISOPOO sinks in the experiments:

- The lifetime of ISOPOO against HO_2 was 5 s for the conditions of Experiment #1, two orders of magnitude lower than the estimated lifetime of gas-phase species against wall collisions.
- Although the absorption spectrum of ISOPOO radicals is not known specifically, oxygen-substituted organic peroxy radicals typically absorb across the range 200 to 300 nm (Lightfoot et al., 1992; Wallington et al., 1992). By comparison, the employed lamps had negligible photon emission for wavelengths shorter than 310 nm (cf. Question #5). Even so, a caveat is that there is at least one case, represented by the $CH_3C(O)CH_2OO$ radical, for which absorption above 300 nm was reported (Cox et al., 1990).
- The results of the high-NO_x experiment (#7) also provide evidence that wall collisions and photolysis were unimportant for the fate of ISOPOO. The yields $Y_{MVK,NO}$ and $Y_{MVK,NO}$ agree with those reported in the literature for a wide range of reaction conditions. This agreement suggests an absence in Experiment #7 of significant ISOPOO wall collisions or photolysis. The lifetime of ISOPOO against NO (0.9 ppb) was 5 s for Experiment #7. Because the lifetime of ISOPOO against HO_2 for Experiment #1 was also 5 s, the logical inference is that wall collisions and photolysis were also unimportant fates of ISOPOO in that experiment.

We include the above points in the revised manuscript.

(5) Was other unwanted photochemistry important? I could find no mention of the lamp output save reference on page 33328 "Within the CMFR, photolysis of H_2O_2 by ultraviolet light produced OH radicals, initiating isoprene oxidation" and from section 2.4 "The one-sun photolysis rates of the MCM model were scaled by 0.3 to match the lower light intensity of the HEC." Nonetheless, lamps suitable for H2O2 photolysis would impact on other species, notably, MVK, MACR and perhaps isoprene. On page 33335 experiments conducted with different residence times are discussed. These are taken to indicate that photolysis of ISOPOOH and IEOPX are unimportant, though the experiment conducted at

longer residence time did result in larger yields of MVK and MACR. The MCM provides photolysis rates, or at least coarse estimates, for ISOPOOH. Could you use your model output to quantify for experiment #1 how much chemistry was initiated by OH, how much by photolysis of other species (MVK, MACR, isoprene, ISOPOOH)? This sort of detail is important when, ultimately, your conclusions depend on precise determinations of quite small MVK and MACR yields.

In the Harvard Environmental Chamber, ultraviolet irradiation is provided by 46 40 W Sylvania 350BL blacklights affixed to the walls (King et al., 2009). The output spectrum of these lamps is negligible for wavelengths shorter than 310 nm. By comparison, isoprene mainly absorbs light shorter than 250 nm. Hence, photolysis of isoprene in the chamber is not an issue.

For MVK and MACR, we carried out control photolysis experiments. Excess cyclohexane was added as an OH scavenger. No significant loss in MVK or MACR was observed when the UV lights were turned on.

MCM modeling suggests that the photolysis rate of ISOPOOH is on the order of 10^4 molecule cm^{-3} s^{-1} in Experiment #1. By comparison, based on Equation 1, the total MVK/MACR production rate is on the order of 10^7 molecule cm^{-3} s^{-1} in Experiment #1. Therefore, the ISOPOOH photolysis rate is a factor of 10^3 lower compared to the MVK and MACR production rate, arguing that the former is not a significant source of the latter. In support of this modeling result, we also conducted experiments at various residence times whose results would be sensitive to photolysis if it were important (Page 33335 Line 4-21). The conclusion is that "*secondary processes seemed to produce significant quantities of MVK and MACR only for τ » 3.7 hr, and shorter residence times such as in experiment #1 produced yields representative of first-generation production.* "

We include the above points in the revised manuscript:

"Ultraviolet irradiation was provided by 46 40W Sylvania 350BL blacklights (UV-A,315-400 nm) affixed to the walls (King et al., 2009)…

Control experiments show that a photolysis sink for MVK (MACR) was negligible, at least for the conditions of the conducted experiments. …"

"Secondary oxidation processes of some isoprene oxidation products of the HO_2 pathway, like ISOPOOH ($C_5H_{10}O_3$) and IEOPX ($C_5H_{10}O_3$), could conceivably also produce some MVK and MACR and therefore represent an additional source term. For example, the MCM suggests that photolysis of ISOPOOH can lead to ISOPO and hence MVK and MACR, although the modeled contribution of ISOPOOH photolysis is <1% of the production rate of MVK and MACR in Experiment #1. As one test of the data against this possibility, experiments were conducted for halved (#2; 1.9 hr) and doubled (#3; 7.4 hr) chamber residence times (relative to 3.7 hr in Exp #1)..."

(6) Another potential interfering source of MVK and MACR products is the presence of small amounts of NO. The authors have taken every measure to minimize NO experimentally, and recorded (below detection limit) values of < 70 ppt. In section 3.3 and table 3 the proportion of ISOPOO reacting with HO_2, with NO and with itself is reported. A value of > 93 % was calculated for ISOPOO reacting with HO_2, with the remainder (<

7 %) reacting with NO. These calculations used literature values for rate coefficients (k) that are highly uncertain. For example, k_1 was obtained from the IUPAC database, based on the sole available measurement of k_1, from Boyd et al. (2003). Consequently, a large uncertainty of $\Delta\log(k_1) = 0.3$, or approximately a factor of two is quoted by IUPAC. There is also some uncertainty in k for ISOPOO + NO, and the value of $[HO_2]$ taken from your MCM simulations. Based on the upper-limit of 70 ppt for NO, and reported uncertainties in the rate coefficients for ISOPOO with HO_2 and NO, I have calculated a lower-limit of 85 % for ISOPOO reacting with HO2. How does this smaller lower-limit propagate into overall uncertainties in MVK, MACR and HO_x yields?

Regarding to steady-state NO concentration, the value stated in the manuscript of 70 ppt is a conservative estimate of the upper limit based on direct detection by the NO sensor, meaning that the actual concentration is expected as significantly lower. As we state in the manuscript, *"Actual NO concentrations were lower because of titration by HO_2, perhaps on the order of 3 ppt based on the model simulation."* The titration effect of NO by HO_2 was tested by adding 0.5 ppb NO into the chamber inflow after steady state was achieved under the same experimental conditions as Experiment #1. As shown in Figure R1, no change was observed in the NO signal (below detection limit) or PTR signals for major product ions, while the NO_x signal (Mo catalyst) increased. The implication is that NO was titrated by excess HO_2 to produce NO_2. This observation is consistent with the MCM simulations, which suggest a steady-state NO concentration of 6 ppt in the presence of an inflow NO concentration of 0.5 ppb due to titration by HO_2. This experimental result is included in the revised manuscript and supplementary material.

We also recognize the uncertainties in the modeling results, as described by the reviewer. On Page 33336, the manuscript states, "*The accuracy of the foregoing modeling analysis is subject to uncertainties in the kinetic scheme of MCM v3.2 and the reaction rate coefficients of isoprene-derived RO_2 via each pathway*." We therefore designed a series of experiments to verify that there was no considerable contribution to Experiment #1 from pathways other than HO_2 (Page 33336). Since the yields of MVK and MACR via the NO pathway (41.5% and 26.5%, respectively, from MCM) are much higher than those measured in Experiment #1 (4.6 ± 0.3% and 3.2 ± 0.2%, respectively), if the NO pathway significantly competed with HO_2, the MVK and MACR yields would have decreased with an increase of the H_2O_2 and hence HO_2 concentrations. *"As shown in Figure 4B, doubling the H_2O_2 concentration (Experiment #5, Table 3) did not decrease the yield significantly compared with Experiment #1. Halving of the H_2O_2 concentration, however, increased the MVK and MACR yields (Experiment #4, Table 3), implying that pathways other than HO_2 made contributions in case of low HO_2 concentration."* The conclusion is that the NO pathways probably accounted for a very small fraction of ISOPOO sink in Experiment #1 because of the high HO_2 concentrations."

As an alternative test, the possible minor contribution of the NO pathway to the yields of MVK and MACR in the HO_2-dominant experiments is estimated by constructing a kinetic model having branching ratios ξ_{HO2} and ξ_{NO} for the fate of ISOPOO with HO_2 and NO, respectively, and then applying a fit of the model to the observed yields from the three experiments using various H_2O_2 concentrations. The model is constructed as follows. In the case that MVK and MACR are produced only by these reactions, $Y_{MVK} = Y_{MVK,HO2}\, \xi_{HO2} + Y_{MVK,NO}\, \xi_{NO}$. For the case of ISOPOO loss only by HO_2 and NO reactions, the branching ratios can be expanded in terms of the relative rates of the two reactions. The measured yield Y_{MVK} of MVK is then as follows:

$$\begin{aligned} Y_{\text{MVK}} &= Y_{\text{MVK,HO}_2} \frac{k_{\text{HO}_2+\text{ISOPOO}}[\text{HO}_2]_{ss}}{k_{\text{HO}_2+\text{ISOPOO}}[\text{HO}_2]_{ss} + k_{\text{NO+ISOPOO}}[\text{NO}]_{ss}} \\ &\quad + Y_{\text{MVK,NO}} \frac{k_{\text{NO+ISOPOO}}[\text{NO}]_{ss}}{k_{\text{HO}_2+\text{ISOPOO}}[\text{HO}_2]_{ss} + k_{\text{NO+ISOPOO}}[\text{NO}]_{ss}} \end{aligned} \qquad \text{(R1)}$$

An analogous equation exists for Y_{MACR}. Terms in Equation R1 include the yields $Y_{\text{MVK,NO}}$ and $Y_{\text{MVK,HO}_2}$ of MVK for the NO and HO_2 pathways, the reaction rate coefficients $k_{\text{NO+ISOPOO}}$ and $k_{\text{HO}_2+\text{ISOPOO}}$ of ISOPOO with NO and HO_2, and the steady-state concentrations $[\text{NO}]_{ss}$ and $[\text{HO}_2]_{ss}$ of NO and HO_2.

Any NO contamination in the chamber is taken to have a zero-order source term $k_{0,\text{NO}}$ independent of reactions conditions. For instance, there can be NO present in the inflow air (i.e., what passes the pure air generator), or NO can diffuse from the outside chamber environment through the walls of the Teflon bag into the reaction zone. Because NO is produced slowly but reacts quickly with the excess HO_2, we invoke the steady-state approximation and write

$$0 = k_{0,\text{NO}} - k_{\text{NO+HO}_2}[\text{NO}]_{ss}[\text{HO}_2]_{ss} \qquad \text{(R2)}$$

where $k_{0,\text{NO}}$ is the production rate of NO and $k_{\text{NO+HO}_2}$ is the reaction rate coefficient of NO and HO_2.

Combining Equations R1 and R2, we have:

$$\begin{aligned} Y_{\text{MVK}} &= Y_{\text{MVK,HO}_2} \frac{[\text{HO}_2]_{ss}}{[\text{HO}_2]_{ss} + \dfrac{k'}{[\text{HO}_2]_{ss}}} + Y_{\text{MVK,NO}} \frac{\dfrac{k'}{[\text{HO}_2]_{ss}}}{[\text{HO}_2]_{ss} + \dfrac{k'}{[\text{HO}_2]_{ss}}} \\ &= Y_{\text{MVK,HO}_2}\left(1 + \frac{k'}{[\text{HO}_2]_{ss}^2}\right)^{-1} + Y_{\text{MVK,NO}}\left(1 + \frac{[\text{HO}_2]_{ss}^2}{k'}\right)^{-1} \end{aligned} \qquad \text{(R3)}$$

where $k' = \dfrac{k_{\text{NO+ISOPOO}}\, k_{0,\text{NO}}}{k_{\text{HO}_2+\text{ISOPOO}}\, k_{\text{NO+HO}_2}}$. An analogous equation (not shown) to Equation R3 also exists for Y_{MACR}.

Regarding Equation R3, known terms include $Y_{MVK,NO}$ as determined in the high-NO_x experiment (#7), Y_{MVK} that was measured, and $[HO_2]_{ss}$ that was simulated by the MCM (Table 3). Unknown terms are Y_{MVK,HO_2} and k'. Experiments #1, #4, and #5 lead to three realizations of Equation R3; the values of Y_{MVK,HO_2} and k' can be numerically optimized to minimize the sum-of-the-square of differences of the equality statement of the three realizations. Similarly, there are three realizations for Y_{MACR,HO_2} and k'. Overall, there are therefore six statements of equality and three terms Y_{MVK,HO_2}, Y_{MACR,HO_2}, and k' that are optimized to minimize the sum-of-the-square of differences. Uncertainty estimates (2σ) in $Y_{\mathrm{MVK,HO_2}}$, $Y_{\mathrm{MACR,HO_2}}$, and k' were obtained by a Monte Carlo method of sampling from the uncertainties in the input parameters and reevaluating the values of the optimized parameters. An uncertainty of 30% was used for the simulated HO_2 concentrations based on uncertainties in reaction rate constants of the dominant source and sink of HO_2.

The fits after numerical optimization are shown in Figure R2. Optimized values are as follows: $Y_{\mathrm{MVK,HO_2}}$ = (3.8 $\pm$1.3)% and $Y_{\mathrm{MACR,HO_2}}$ = (2.5 $\pm$0.9)%. The steady-state NO concentrations, corresponding to the obtained k' value ($7.5^{+14.1}_{-4.9} \times 10^3$ ppt^2), are 21^{+31}_{-13}, 14^{+26}_{-9}, and 9^{+21}_{-6} ppt for the conditions of half, reference, and double H_2O_2, respectively. For these results, Equation R3 implies that the branching ratios of ISOPOO to the HO_2 and N O pathways are 0.97 and 0.03, respectively, for Experiment #1.

The above analysis is included in the revised manuscript.

(7) In table 3 and the text regarding the fate of ISOPOO, the unimolecular rearrangement proposed by Peeters et al. has been neglected. There is considerable dispute as to the importance of this process, with the 2009 Peeters calculations reporting a rate of around 1 s^{-1}, and Crounse et al. (2011) subsequently deriving a value of 0.002 s^{-1} from experimental observation. Nonetheless, it is surely worth noting this controversy given the rate for (R1) of $k_1[HO_2] \approx 0.2\ s^{-1}$ in experiment #1 in this work.

Unimolecular rearrangement (isomerization ISOM in Table 3 and its footnotes) was considered using the reaction rate coefficient (0.002 s^{-1}) from Crounse et al. (2011). The resulting estimate of its contribution to the fate of ISOPOO was 0.8% for Experiment #1. Using the bulk isomerization rate coefficient (0.01 s^{-1}) provided by Peeters and Mueller in their comments posted in the online discussion forum of this article, the contribution of isomerization to the fate of ISOPOO is 4%.

As proposed by Peeters et al. (2009), ISOPOO can undergo two types of isomerization reactions, i.e., 1,6-H-shift and 1,5-H-shift. 1,6-H-shift leads to the formation of unsaturated hydroperoxy aldehydes (HPALDs), and 1,5-H-shift leads to the formation of MVK and MACR. Experiments by Crounse et al. (2011) confirmed the formation of HPALDs with a reaction rate constant of ~ 0.002 s^{-1}, but there has been no clear laboratory evidence for the formation of MVK and MACR from the isomerization of ISOPOO. According to the prediction by Peeters and Muller (2010), the primary yields of MVK, MACR and HPALDs via the isomerization pathway are 15%, 9%, and 76%, respectively.

As a test run, the isomerization term was included in Equation R1 using the product yield and higher rate constant from Peeters and Muller (2010). The resultant MVK and MACR yields via the HO_2 pathway were 3.5 % and 2.4 %, respectively, which are -0.3 and -0.1 lower than the yield value otherwise and thus within the stated uncertainty of the results. As a caveat, the accuracy of this analysis is subject to the uncertainties of the reaction rate coefficients and product yields.

(8) My primary concern with this paper is that the uncertainties reported for MVK, MACR and HO_x yields are extraordinarily small. Very little detail is given about how such uncertainties were estimated. The supplemental info gives two short paragraphs describing error analysis using a Monte method. I would move this to the main text, and include more detail with numerical examples in an extended supplemental info. Please state in the main text whether uncertainties are 1 or 2σ. Please give some idea as to whether these are principally derived from data scatter, or from systematic errors in the experiment (calibrations etc.) or the documented uncertainties in literature parameters. Without a more detailed treatment of errors the reader simply cannot assess how robust these results really are.

We thank the reviewer for this input. The uncertainties in the original text were 1σ; they are updated to a 2σ representation in the revised text.

Additional uncertainty analysis has been done using the Monte Carlo method. The uncertainties in all the input parameters in Equations 2 and 3 are now taken into account, including both the uncertainties in concentrations and chamber residence times (original manuscript) and the reaction rate coefficients (updated manuscript). The uncertainties in the concentrations are based on calibrations. The uncertainties in the reaction rate coefficients are obtained from the IUPAC recommendation. A 6% 2σ-uncertainty is used for the chamber residence time based on the standard deviation in measured residence times for multiple experiments. Table R1 presents an example of the inputs and outputs of the uncertainty analysis for Experiment #1. The reported yields of MVK and MACR in Experiment #1 were respectively reported as (4.6 ± 0.3) % and (3.2 ± 0.2) % (1σ) in the original manuscript and are reported as (4.6 ± 0.7) % and (3.2 ± 0.6) % (2σ) in the revised manuscript.

A description of the uncertainty analysis is included in the revised text, as follows,

"Yields of MVK and MACR for each experiment are listed in Table 1. In the case of Experiment #1 for HO_2-dominant conditions at 25 ℃ and < 2 % RH, the MVK and MACR yields were (4.6 ± 0.7) % and (3.2 ± 0.6) %, respectively. The uncertainties (2σ) in Y_{MVK} and Y_{MACR} were estimated using a Monte Carlo method in which the values of all input parameters in Equations 2 and 3 were sampled from probability density functions of their individual values (i.e., their individual uncertainties). An example of the input and output uncertainties is presented in the Table S1. The uncertainties in the concentrations were based on calibrations. The uncertainties in the reaction rate coefficients were obtained from the IUPAC recommendation. A 6% 2σ-uncertainty was used for the chamber residence time based on the standard deviation in measured residence times for multiple experiments. The ensembles of results for Y_{MVK} and Y_{MACR}, which can be approximated by a normal distribution (Figure S4), were the basis of the reported statistical errors in the mean values."

(9) I appreciate that the determinations of MVK and MACR concentration were of high precision. Nonetheless, from the data presented in Table 1 these were not insignificant, eg. for experiment #1 at steady-state (1.3 ±0.1) ppb for MVK and (0.8 ±0.1) ppb for MACR. Product yields were determined via equation 2 which contains terms such as rate

coefficients, radical concentrations and wall-loss rates, resulting in yields for MVK of (4.6 ±0.3) % and for MACR (3.2 ±0.2) %. I would have expected the reported errors to increase as the calculations get more complex and more uncertain parameters are included, but the opposite is the case here. How can this be justified?

This issue is related to the rounding of the concentration and uncertainty values given in Table 1. For all the values in Table 1, one decimal point was shown. The actual MVK and MACR concentrations have higher precision. For example, (1.3 ± 0.1) ppb (1 σ) of MVK and (0.8 ± 0.1) ppb of MACR shown in Table 1 (Experiment #1) correspond to (1.29 ± 0.07) ppb of MVK and (0.79 ± 0.05) ppb of MACR. The calculated yield values of MVK and MACR are (4.62 ± 0.27) % and (3.246 ± 0. 248) %, respectively, so that (4.6 ± 0.3) % and (3.2 ± 0.2) % were shown in Table 1. Hence, the relative uncertainties of the calculated yields do increase compared to those of the measured concentrations.

By updating the uncertainties from 1σ to 2σ in the revised text, the above issue is clarified.

(10) Ultimately a yield for HOx recycling of "15 ±0.7%" is reported − uncertainty 1/20 of absolute value - even though this is dependent on the original MVK and MACR concentrations (precision ~ 1 / 10) and a whole host of other parameters in model simulations. As noted above (for k_1), some of these parameters are associated with large uncertainties. I can see that reliance on model simulation via the MCM is necessary, however where the results are dependent upon a critical parameter this should be highlighted, especially if data are in short supply. More discussion of assumptions made regarding the fate of ISOPOO is needed. As I see it, the yields reported in this work rely on results from Boyd et al. (2003) and Crounse et al. (2011) being substantially correct, and those of Peeters et al. (2009) being wrong. The reader should be left in no doubt about this.

We thank the reviewer for this suggestion. In the revised manuscript, a new section (3.4) is added to describe how the yield of MVK and MACR via the HO_2 pathway is determined from the experimental results. The contribution of the NO pathway is taken into account by fitting experimental data at varying H_2O_2 concentrations (cf. Question #6). The potential contribution of the isomerization pathway is small even when the higher reaction rate coefficients suggested by Peeters et al. (2009; 2010) is used (cf. Question #7). The other possible competing pathways suggested by the reviewer, including wall loss and photolysis of ISOPOO, are not directly treated, as now noted in the revised manuscript (cf. Question #4).

In the original manuscript, the yields of MVK and MACR via the HO_2 pathway were estimated by averaging the yields of all the valid HO_2-dominant experiments, including Experiment #1, #2, #5 and #6 (cf. Table 3), assuming 100% of ISOPOO reacted via the HO_2 pathway in these experiments. The resultant values, (4.3 ± 0.4) % and (3.2 ± 0.3) % [1σ uncertainties, original analysis], represent upper limits of the yields via the HO_2 pathway. In the revised manuscript, a best estimate is obtained by fitting the experimental data to constrain the contribution of the NO pathway (cf. Question #6). The revised best estimates of MVK and MACR yields via the HO_2 pathway are (3.8 ± 1.3) % and (2.5 ± 0.9) % [2σ uncertainties], respectively.

(11) Incidentally, the notation used for reporting uncertainty in yields throughout the manuscript is confusing. It may be best to clarify in the abstract that these are "percentage yields for MVK and MACR of 4.3 ± 0.4 and 3.2 ± 0.3" or include parentheses as I have

above, eg. "(4.3 ± 0.4)% and (3.2 ± 0.3)%". For the radical recycling yield I suggest you differentiate between an OH recycling yield of ~7 % and your overall HO_x recycling yield (15 %). I also strongly suggest you revise upwards the uncertainty in these parameters.

We thank the reviewer for this suggestion. The uncertainties are revised to the format of (4.3 ± 0.4) %. Please refer to Questions #6, #8, and #10 for the revised estimate of the uncertainties. The OH and HO_2 recycling yield are now reported separately in the revised manuscript, (6.3 ± 2.1) % for each, and a total HO_x recycling yield of (12.6 ± 4.2)% is also reported.

(12) Figure 1 displays isoprene oxidation pathways as reported by the MCM. My understanding is that these relative yields of ISOPOO A, B, C and D are the nascent or kinetic yields following O2 addition, appropriate for conditions where the lifetime of ISOPOO is << 1 s. In polluted air, and in previous chamber experiments such yields are appropriate. However, Peeters et al. (2009) report that "repetitive O2 addition/elimination will continuously interconvert the three O2-adduct isomers / conformers of a given OH-isoprene radical—leading to steadystate populations approaching equilibrium and so channel the bulk of the reaction flux through the fastest product forming route." Therefore in conditions of ISOPOO lifetime > 1 s, such as real clean-air, and also in your experiments, a different "equilibrium" distribution of ISOPOO applies. Please note that this equilibration of ISOPOO is not the controversial aspect of Peeters' Leuven Isoprene Mechanism. For further reference see the discussionin Peeters et al. (2009), Peeters and Müller (2010), Nguyen et al. (2010), Crounse et al.(2011), and references therein.

Happily for the conclusions of this work, ISOPBOO (32 %, producing MVK) and ISOPDOO (60 %, producing MACR) dominate the equilibrium distribution. Peeters' statement that the bulk of reaction proceeds via the fastest product route is redundant here providing that 1) the k1result from Boyd et al. (2003) applies to all ISOPOO, an assumption adopted in this work and in the MCM. 2) that the subsequent intramolecular rearrangements proposed by Peeters et al. (2009) do not apply, ie. are slower than reported. This assumption has also implicitly been applied when Interestingly, if the equilibrium distribution and subsequent assumptions apply, then approximately a factor of two larger MACR than MVK yields would be expected. This was not observed from the experiments in this work. Does the observed ratio MVK:MACR of 4:3 from both the HO2- and NO-dominated experiments provide evidence fora different equilibrium ISOPOO distribution? It is close to what would be expected from nascent / kinetic ISOPOO. Or are the larger MVK:MACR ratios reported in this work a result of secondary chemistry? It would be worth running a quick simulation using the Peeters rate constants for HO-ISOP + O2 <-> ISOPOO, and your experimental estimates of [HO2] and [NO] to establish whether you are fully in the equilibrium regime in all experiments.

Dr. Dillon provided a personal communication to us that this question is withdrawn in light of the comments posted by Peeters and Muller in the online discussion forum of this manuscript.

(13) Finally, a few points concerning the atmospheric implications section, and Figure 2. In the caption to Figure 2 it should be noted that unimolecular decomposition of ISOPOO may be important in unpolluted conditions, as proposed by Peeters et al. This is even if Crouse et al. are correct, and the unimolecular rate is slower than Peeters first reported.

Crounse calculate up to 20 % of ISOPOO lost to the unimolecular process in rainforest conditions; 7-10 % globally, even using the much slower rate.

We agree with the reviewer. Figure 2 and Figure 5 (comparison with other laboratory yield data) in the original manuscript are combined together as one figure (Figure 5 in the revised manuscript). The revised caption regarding original Figure 2 is as follows:

"The inset triangle diagram represents environmental factors that can affect the dominant reaction pathways of isoprene-derived ISOPOO radicals in the atmosphere and in the laboratory studies. The isomerization pathway is not included in the diagram due to its small contribution in most laboratory studies, although it could be important under remote atmospheric conditions. "

(14) The final sentence "Another possibility, suggested by a recent report on instrumental issues, could be that the gap between measured and modeled OH was not so large as originally reported (Mao et al., 2012)." I see what you are getting at here, but apply caution, as it is hazardous to extrapolate from one set of campaign conditions to another. Or indeed from one instrument to another. However, it is worth noting that the paper by Mao suggests that OH was over-reported in some forest conditions. Strictly speaking the gap between measured and modeled OH was what it was; perhaps the gap between an ideal OH measurement and the model would not be (as) large, but we don't really know.

We agree with the reviewer. The sentence is revised as follows:

"As suggested by a recent report on instrumental issues, the gap between actual and modeled OH may not be as large as originally reported in some studies (Mao et al., 2012)."

(15) There is a rare typo on page 33326 line 6 "hyrotetroxide".

The correction is made in the revised manuscript.

Reviewer #2

Liu et al. describe recent experiments designed to probe the photochemistry of isoprene oxidation by OH under NO starved conditions. They suggest small yields of methacrolein (MACR) and methyl vinyl ketone (MVK) are produced from the reaction of isoprene hydroxy peroxy radicals with HO2.

This is an important study with implications for atmospheric analytical chemistry. The authors show that signals in PTRMS that have traditionally associated with MACR and MVK can be produced via ionization of the isoprene hydroxy hydroperoxides. The experiments performed – including those using model hydroxy hydroperoxides – are of high quality. This will require a critical re-evaluation of other measurements using PTRMS and conclusions derived from such measurements (such as estimates of MVK/MACR fluxes).

We thank the reviewer for the helpful comments.

(16) The main criticism I have of the study is that the estimate of the uncertainty in the yields of MVK/MACR from the $RO_2 + HO_2$ reactions is unrealistically small. Unfortunately, sensitivity of the instrumentation used was not capable of constraining the

[NO] to better than 70 ppt and as such a significant fraction of the RO_2 loss may have resulted from NO chemistry. Attempts to estimate this fraction using models is problematic given the uncertainly in rates and products of the associated reactions (e.g. HO_2 + RO_2).

Reviewer #1 also highlighted this important topic. In that regard, please refer to Question #6 of this response to reviews.

(17) In the absence of a measurement of NO, do the authors have any information on the production of alkyl nitrates? These can provide a rather direct estimate of the NO chemistry.

We did not observe any identifiable signals of alkyl nitrate parent ions. The only nitrate-containing ion observed in the high-NO_x experiment (Experiment #7) was the protonated ion of peroxyacetyl nitrate ($C_2H_4NO_5^+$) (Hansel and Wisthaler, 2000). This ion was absent in the low-NO_x experiments, as shown in Figure R3. This point is included in the revised manuscript, as follows:

"…Another line of evidence is that the protonated ion of peroxyacetyl nitrate ($C_2H_4NO_5^+$) (Hansel and Wisthaler, 2000), a nitrate-containing ion observed in the high-NO_x experiment (Experiment #7), was absent in all other experiments (Figure S5)."

(18) As it stands, I suggest that authors perform a critical sensitivity analysis of the possible yield of MVK and MACR from NO in their chamber and report the yield of MVK/MACN from the HO2 channel with the appropriate limits (e.g. 15 +- 0.7% recycling will probably be 12 +3-5%;

Reviewer #1 also requested this analysis. Please refer to Question #10 and #11 of this response to reviews.

(19) this also assumes 0 recycling in the delta channels which may or may not be true).

The OH yield we inferred from the measurements is a concomitant OH yield with MVK and MACR production from ISOPBOO and ISOPDOO. This yield can be distinguished from the total yield of OH via the HO_2 pathway. This aspect is clarified in the revised text:

"…Therefore, the MVK and MACR yields via the HO_2 pathway, (3.8 ±1.3) % and (2.5 ±0.9) %, imply a concomitant yield of hydroxyl radical from the ISOPBOO and ISOPDOO channels of R1b of (6.3 ±2.1) %. The total OH yield from R1b could be higher because the ISOPAOO and ISOPCOO channels, which do not produce MVK or MACR, are not evaluated here. "

(20) Finally, I believe that recycling in RO_2 + HO_2 chemistry has also been reported by Wallington and co-workers in halogen substituted 'Rs'.

We thank reviewer for this input. The work by Wallington and co-workers is cited in the revised manuscript. Please refer to Question #1.

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Table R1. Uncertainty Analysis of MVK and MACR yield in Experiment #1 [1]

Input Variables [2]						Output Variables [2]	
Concentrations (ppb) [3]		Reaction rate coefficient, *k* (molecule^{-1} cm^3 s^{-1}) [4]		Others		Yield (%)	
$[C_5H_8]_{in}$	59.3±2.4	$\log_{10}(k_{C5H8+OH})$	-10.00±0.06	τ (hr) [5]	3.7±0.2	MACR	3.2±0.6
$[C_5H_8]_{ss}$	16.0±0.6	$\log_{10}(k_{MACR+OH})$	-10.54±0.10	k_{wall} (s^{-1}) [6]	0	MVK	4.6±0.7
$[MACR]_{ss}$	0.79±0.10	$\log_{10}(k_{MVK+OH})$	-10.70±0.10				
$[MVK]_{ss}$	1.29±0.14						

[1] A Monte Carlo method was used for error analysis. All the input variables in Equation 2-3 were taken into consideration (cf. Equation 1-3 for the definitions of the input variables).

[2] (Mean ± 2 × Standard Deviation) for all the input and output values.

[3] Uncertainties in concentrations were determined by calibrations.

[4] Reaction rate coefficients and their uncertainties were from IUPAC recommendation in common logarithm.

[5] A 6% (2σ) uncertainty was used for residence time based on the standard deviation in measured residence times for multiple experiments.

[6] A value of k_{wall} = 0 s^{-1} was used based on the results of wall-loss experiments (cf. supplementary material).

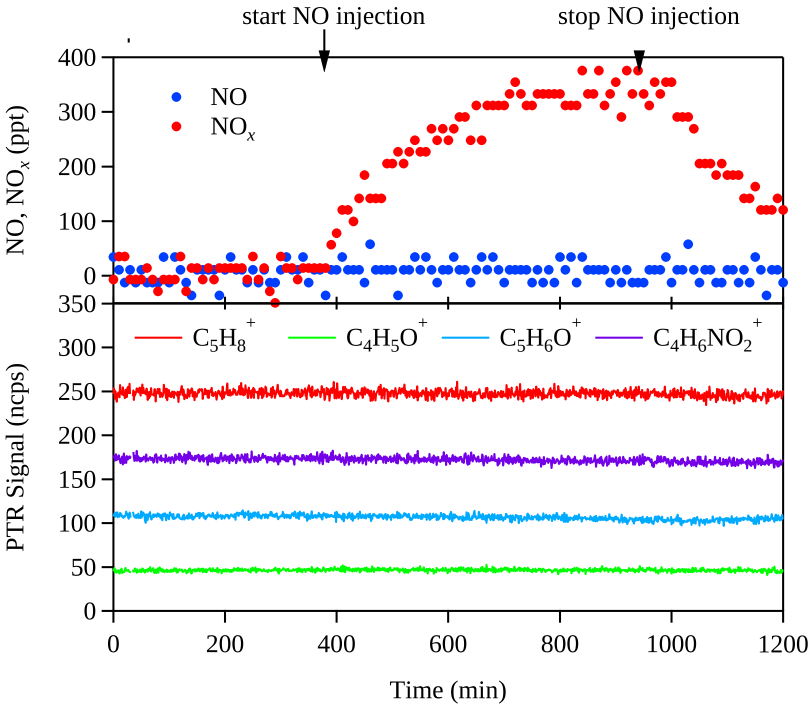

Figure R1. Change in NO, NO$_x$ (top panel) and PTR ion signals (bottom panel) after adding 0.5 ppb NO into the chamber inflow at the steady state of a HO_2-dominant experiment. The experimental condition was the same as Experiment #1. The PTR signals were measured at a trap temperature of 25 ℃ in NO^+ mode.

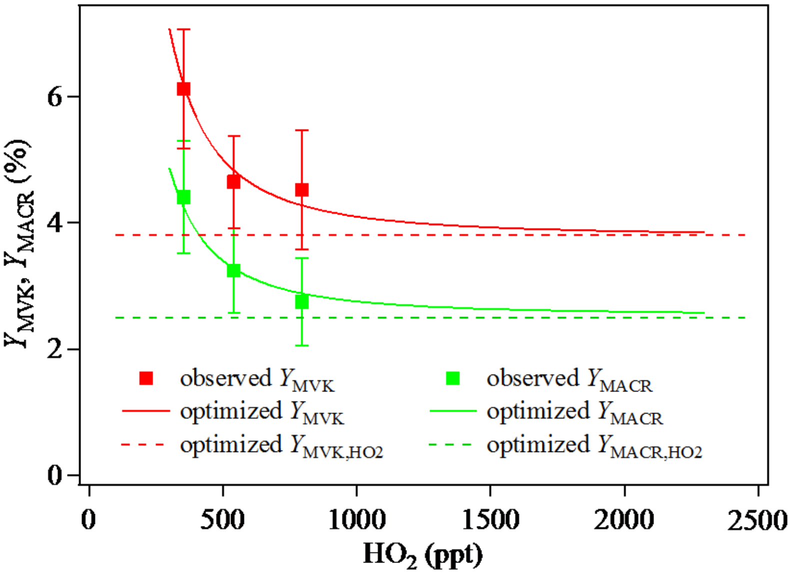

Figure R2. Optimization and sensitivity of Y_{MVK,HO_2} and Y_{MACR,HO_2} by Equation R3 to the yield data of MVK and MACR.

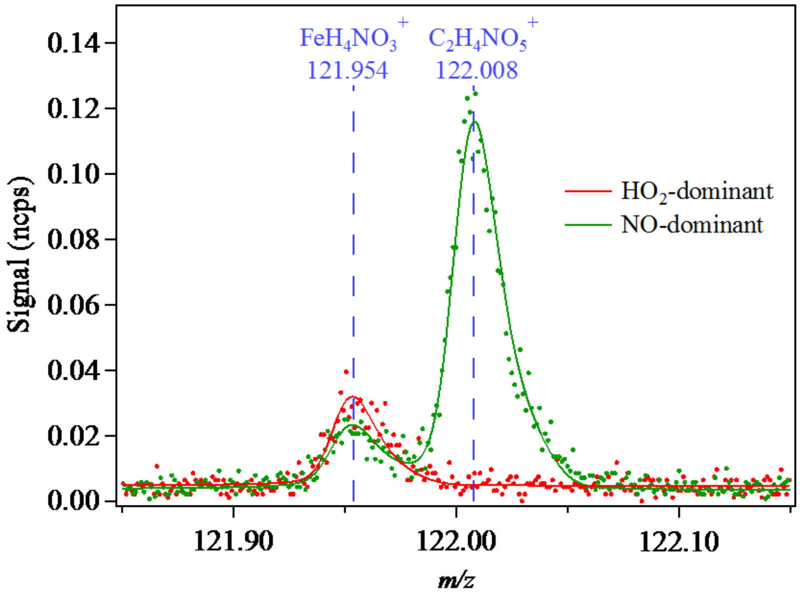

Figure R3. Spectrum comparison of $PANH^+$ in HO_2-dominant (#1) and NO-dominant (#7) experiments. The PTR spectrum were measured at a trap temperature of 25 ℃ in H_3O^+ mode and averaged for 24 mins.