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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Yields of oxidized volatile organic compounds during the OH radical initiated oxidation of isoprene, methyl vinyl ketone, and methacrolein under high–NO_x conditions" *by* M. M. Galloway et al.

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The authors thank the reviewer for his comment, which have improved the manuscript. We have made changes to the manuscript according to the referee's suggestions. Responses to individual comments are below in italics.

This paper described measurements of oxidized products, notably glyoxal (GLX) and methylglyoxal (MGLY), during the oxidation of isoprene, methyl vinyl ketone (MVK) and methacrolein (MACR). The experiments were carried out at the Caltech environmental

chamber. The results demonstrate quite convincingly for the first time that glyoxal can be formed as a primary product in the oxidation of isoprene. This observation, along with associated measurements using mass spectrometry, allow some constraints on proposed mechanisms of isoprene oxidation. The measurements appear to have been carefully done. The novel part of the paper is the use of laser-induced phosphorescence to measure GLX and MGLY in conjunction with other, more conventional techniques. The demonstration of the method is noteworthy. However, the paper requires a little more detail before it comes up to the standard that is required of laboratory determinations, such that other workers will later be able to reproduce or possibly reinterpret the data as needed. In particular, I would prefer to see plots showing some of the other chemical species in a couple of places to verify the chemistry. The writing is also a little terse (e.g. page 10703, lines 22-27), and could use some separation of ideas.

Comments: Other than on page 10704, line 8, I didn't notice any mention of the supplemental figures and table in the text. The text should contain some pointers to the supplemental material (e.g. the discussion of the OH concentration on page 10700).

Thank you. We have expanded the explanations of the supplemental material and improved the references to the supplement.

The experiments last for upward of 8 hours. Please give details of the NO, NO2 and O3 concentrations, especially in the later stages of the runs. At what point was the isoprene depleted?

We have added more explanations of this in the text and have added a figure (Fig. S1) with many of the relevant species for a typical experiment.

Was HONO added continuously to the chamber, or just at the beginning?

HONO was only added at the beginning or the experiments, we have clarified this in the text.

There are some general statements regarding the quality of the fits of MGLY and gly-

colaldehyde, but it would be nice to see somewhere a composite ïňĄgure with loss of starting material, production of major and minor products, and model ïňĄts for a typical run.

We have added a figure (Fig. S5) of an isoprene oxidation experiment with both model and measurement.

Page 10701, line 13: should be Table 2?

Page 10702, line 9: Atkinson et al (1989) should be (1990b) for methacrolein.

Page 10702, line 9: Check the yields from Paulot. Table 2 gives 20% for hydroxyaceÂňtone and 0% for MGLY, but you say their MGLY is much higher than yours. Should also be 20%?

Page 10703, line 13: Define MBO here.

Each of these errors has been corrected. Thank you for pointing them out.

Page 10703, line 23: the modelled glycolaldehyde [from MVK] appears to be less than the measurements, not more. Also, it says that measured methyl glyoxal (not shown) is double modeled concentrations, but in Table 2 the MGLY yield (27%) is identical to the MCM value (29%).

Similar comment for MACR. I think you may be referring to the final value, but again without a figure it's hard to know.

This text has been replaced with the following and a figure has been added to the supplement for a methacrolein experiment: "For the MVK high-NOx oxidation experiments, predicted glyoxal (Figure 3) agrees very well with measurement, and modelled glycolaldehyde and methylglyoxal only slightly exceed the measurements. Measured hydroxyacetone is approx. 75% of modelled in the later part of the experiment, and modelled methylglyoxal is approximately double measured in the later part of the experiment (see Fig. S6)."

Page 10705: I am not surprised that the GLX yields from the C5 carbonyls are less than in the MCM. Berndt and Boge [J. Phys. Chem. A. 111, 2007, 12099-12105] studied the oxidation of 4-hydoxybutenal and found only 17% glyoxal. This is evidence that the majority of the oxy radicals decompose to HCO and a dihydroxy aldehyde, rather than to GLX. So, I would suspect that the yields of GLX and MGLY from C5 hydroxycarbonyls are less than 50% but, in reality, probably greater than zero.

We agree that these yields are probably greater than zero, and that the fact that the model performs best when they are set to zero indicates a need for further study on these compounds. We believe the C5 hydroxy carbonyl chemistry represent a major uncertainty in isoprene chemistry. For our experiments it is hard to evaluate the contribution from C5-hydroxycarbonyls. As we have no reliable measurements it is hard for us to quantify this reliably. We have rephrased all discussion of the C5 hydroxycarbonyls.

Furthermore, the rate constants used in the MCM for OH + C5 carbonyls look low. A more rapid reaction (say 2x) might make it more difïňĄcult to distinguish between primary and secondary GLX production. A little extra modeling should be done to test this.

The rate constants may indeed be low. In response to this suggestion, we increased the C5 carbonyl rate constants by up to a factor of 4, but this did not bring the model into agreement with measurement without also decreasing the yield.

Table 2: The yields listed for hydroxyacetone from MVK should be for methylglyoxal (25% from Tuazon, and 26.5% from Paulot). The yield of MGLY from MACR inferred by Paulot et al. should be 20%? The yield of MGLY from MACR in the MCM should be 8%, not zero.

These errors have been corrected. The MCM v3.1, which we had been using, as MCM v 3.2 was not available, did not have a direct yield of MGLY from MACR. We have incorporated the direct yield of MGLY from MACR for MCM v3.2 into both the table and

model with the new model runs from v 3.2.

Supplement, Fig S4: The yield of MGLY from MACR is here given as 15%.

Thank you. This has been corrected. The correct value is 8%.

Overall a good paper, but needs more data in the Figures in order to be able to assess potential problems with secondary chemistry. Also, the information in the Supplemental file needs to be referenced in the paper and explained a little better.

Both the figures and supplemental material have been re-evaluated with this in mind. A figure has been added with more information about each compound over the course of the experiment, and the supplemental section has more explanations and is referenced in the paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 10693, 2011.