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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.

M. M. Galloway et al.

galloway@reed.edu

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The authors thank the reviewer for their comments and have made changes to the manuscript according to the referee's suggestions. Responses to individual comments are below in italics.

This paper provides experimental data convincingly showing the production of small yields of glyoxal, glycolaldehyde and hydroxyacetone as first generation products from isoprene. They also report first generation methylglyoxal formation from MVK and

MACR. Gas-phase glyoxal was continuously monitored using a laser induced phosphorescence instrument and chemical ionization mass spectrometry (CIMS) was used for on-line measurement of gas-phase glycolaldehyde and hydroxyacetone.

The authors included their data in the Master Chemical Mechanism (MCM) improving its initial performance. Further improvement of the MCM resulted from lowering the first generation glyoxal production from C5 carbonyls (hydroxcarbonyls??), suggesting the importance of further experimental data on the fate of these C5 carbonyls. This is an important study, but its presentation could be improved by including additional experimental details. Specific comments that should be addressed are as follows:

p. 10396, lines 24-26: The authors mention the upper limit of Orlando et al. (1999) for methylglyoxal from MACR, they should also note the yield measured by Tuazon and Atkinson (1990b).

This wording has been changed to "Based on their detection limit for methylglyoxal, they were also able to infer an upper limit for the first–generation methylglyoxal yield from MACR.", and the yields of Orlando et al. (1999) and Tuazon and Atkinson (1990b) are now mentioned in another paragraph.

p. 10697: The authors should provide more details concerning the experimental methods: Were the lights black lamps? What NO2 photolysis rate did 100% lights correspond to? What were the initial HONO concentrations? At what stage during the experiment did O3 formation begin? What were the total irradiation times?

This section has also been expanded to include more information on the experimental conditions and procedures. Initial HONO concentrations are not known, but we were able to calculate initial OH concentrations for each experiment, and they were consistent between experiments. A figure has also been added for a typical experiment that shows typical OH, NO2, NO, and O3 concentrations throughout the experiment.

p. 10698, line 3: the units for the limit of detection for glyoxal are not clear, why are

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they in ppt s-1? For 30 s time resolution, what is the limit of detection in ppt?

We thank the reviewer for pointing this out and have changed the LOD of glyoxal to 2.9 ppt in 30 s.

p. 10698, lines 7-8: since the paper describing the "lifetime methylglyoxal detection method" is in preparation, a brief description of the method would be useful for the reader.

The lifetime detection method speciates glyoxal and methylglyoxal by exploiting the difference in their time-dependent distribution of phosphorescence photons, an exponential decay, after excitation by a light source. This technique allows for differentiation with a single wavelength. The unique phosphorescent lifetimes of these molecules allow sample decays to be fit to a linear combination of these two decays as well as a constant background which accounts for PMT dark counts, laser scatter, and any ambient light which has reached the detector. The fitted prefactor of each ideal decay is proportional to its respective chemical. Limits of detection of 11 ppt and 269 ppt in 5 minutes (3σ) for glyoxal and methylglyoxal, respectively, are achieved with this method. We have added a brief section on this in the supplement and a manuscript is being submitted to Atmos. Meas. Techn.

p. 10701, line 5-7, this sentence needs clarification: I assume the authors mean that because MACR and MVK are less reactive than isoprene the reactions of products are more apparent earlier in the MACR and MVK reactions than in the isoprene reactions.

The reviewer is correct. We are referring to the rate of reaction and the speed at which the first generation products react upon formation. As this is confusing, and the process by which we determined first generation yields was still very similar to the process we used for isoprene, we have changed our calculations to use a linear relationship for all species. The length of the line is shorter in some cases, but this method works for all the species we studied. We have clarified this section as it is an important aspect of the manuscript.

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p. 10701, equation 3, is there any theoretical basis for this equation or is it merely empirical?

This equation was empirical.

p. 10701, line 28: I suggest that the authors replace “this” with the “Dibble mechanism”.

Thank you. We have made this change.

p. 10702, lines 9 and 10: The entry from Paulot et al. (2009a) for methylglyoxal from MACR in Table 2 is 0% -either this entry is incorrect, or the statement on lines 9-10 is incorrect. Also on line 9, the “and Atkinson (1989)” should be “and Atkinson (1990b)”. p. 10704, line 12: Again a problem with the entry from Paulot et al. in Table 2 being inconsistent with the text.

The error in Table 2 has been corrected as well as the incorrect reference. Thank you for bringing these to our attention.

p. 10705, line 5 onward: I assume the C5 carbonyls are, in fact, C5 hydoxycarbonyls. With regard to reactions of C5 hydroxycarbonyls, Berndt and Boge (J. Phys. Chem. A, 2007 111, 12099) measured glycolaldehyde and glyoxal yields from OH + 4-hydroxy-2-butenal of 40 +/-6% and 17 +/-4%, respectively. Baker et al. (Envir. Sci. Technol., 2005, 39, 4091) observed glycolaldehyde from OH + 1,3-butadiene and ascribed it to essentially unit formation from OH + 4-hydroxy-2-butenal. These apparently conïňĆicting observations may be reconciled, at least in part, if glycolaldehyde is also formed as a ïňĄrst generation product from OH + 1,3-butadiene.

The reviewer is correct. The C5 carbonyls are C5 hydroxycarbonyls. We have added their MCM designations (HC4ACHO and HC4CCHO) to the manuscript, and have taken into account the studies mentioned above in adjusting the yield of glyoxal and glycolaldehyde from these compounds. However, removing these pathways altogether still brings the measurement and model into closest agreement, indicating that more work needs to be done on these species.

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Table 1: “C1” should be footnoted as data from Chan et al., 2009?

That is correct. We have added a footnote.

“Table 3” appears in the text when referring to both Table 2 and Table 3.

Thank you for pointing this out. We have corrected the references.

Table 2 provides very important values, some of which appear to be in incorrect columns. The first line of data for isoprene, MVK and MACR should be footnoted as the experimental values from this work (if this is correct). In the table title: are these “molar” yields? For MVK in Table 2, what is presently listed as hydroxyacetone yields for the Tuazon and Atkinson and Paulot et al. entries are the methylglyoxal yields. For the present work listed in Table 2 (and in the text, e.g., p. 10701, line 15) what are the error limits (for example, 1 or 2 standard deviations or what).

Thank you for these suggestions. We have added footnotes to indicate experimental yields and have clarified that we are presenting molar yields. The hydroxyacetone yields have been corrected in the table. All yields are listed with 1 sigma error.

A more descriptive Table caption on Table 3 is necessary to avoid confusion.

We have changed this caption to read “Total molar yields from isoprene oxidation with OH calculated with the modified MCM for high NOx conditions. Total yields are calculated by allowing the model to run until species of interest have been reacted away.”

Figures 2 and 3, it would be useful if the yields of the various model parameters (for example, the yields of products modeled) were given in the figure caption.

Thank you. This has been added.

Figure 4, line 2 of caption, I suggest the authors replace “attenuated” with adjusted or some other verbiage.

This suggestion has been implemented.

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Most of the information in the Supplement is not referred to in the manuscript.

Thank you. We have corrected this, and now refer to the entire supplement in the main manuscript. We have also expanded the supplement to be clearer.

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

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Interactive Comment