

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 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 concerns the detection of products at various stages in the degradation pathways of OH initiated oxidation of isoprene, MACR and MVK under very high levels of NO_x in a chamber. The novelty lies in the in situ optical detection of glyoxal

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and methylglyoxal using laser-induced phosphorescence spectroscopy, combined with detection of other products (glycolaldehyde and hydroxyacetone) and reactants using mass spectrometric and gas chromatographic methods. The combination of analytical techniques is a strength of the paper. The formation of first generation products are separated from products formed from break-down of intermediates using correlations of product formed versus depletion of reagents, and deviations from linearity. The yields are incorporated into the Master Chemical Mechanism which is then used to simulate other species, and comparison made. It was found that the yield of glyoxal from C5 carbonyls had to be reduced significantly from values in the MCM in order to reproduce the glyoxal time-series at longer times in the experiments.

There seems no doubt from the time-dependence of the data (product formation versus reactant loss) that the glyoxal is formed directly from OH+isoprene as a first generation product, with a low yield of about 2.3%, with the necessary corrections having been made. Although the procedure is listed fairly carefully, it was difficult to follow the text in places. Some details are missing, for example the concentration of HONO used to make the OH, the wavelengths from the lamp which photolysed this to form OH, and although initial concentrations are listed (e.g. NO_x in table 1), the change in these concentrations throughout the experiment are not given (maybe need some more plots of this). The NO_x levels really are quite high. Would the conclusions be the same for a few ppb of NO?

We have added more details to the experimental section, which make the conditions under which the experiments were run clearer. We have also added a plot of many of the compounds of interest (including NO_x) for a typical experiment. Several experiments were run (see Table S1) with only a few ppb of NO, and the model reproduces these experiments as well, so we believe that we can draw the same conclusions at lower NO levels. However, questions remain as to whether or not long lifetimes of RO2 might be active at low NO levels, such as in the Peeters/Leuven mechanism (Peeters et al., 2009), which could potentially change this.

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Figures S1 to S3 do not seem to be cited from the text. The supplementary info is just figures, captions and tables, with no text to go with it – hence this is quite an isolated section, and it is not clear how it integrates with material in the main paper. I found Table S2 a little difficult to take in, and the classifications are very subjective, what is excellent agreement for example?

Thank you for pointing this out. We have corrected this issue and added both references to the supplemental figures and text within the supplement. Table S2 has been changed to be more quantitative.

Detailed comments.

Put the primary yield of glyoxal from isoprene in the abstract, an important result obtained directly.

Thank you for the suggestion. We have incorporated the yield into the abstract.

I found Leeds MCM and NCAR MCM confusing – say a few words on how these are different.

The Leeds Master Chemical Mechanism and the NCAR Master Mechanism are both chemically explicit mechanisms of gas phase atmospheric compounds that are used for atmospheric modeling. Different groups maintain them; the Leeds MCM has been recently updated (2011), the last update to the NCAR Master Mechanism was in 2005.

The RH is quite low in the experiments -comment about not expecting the results to be sensitive to this parameter.

We do not expect this gas phase chemistry to be sensitive to RH, and have changed the text to state that “The reactions studied here are not expected to be sensitive to RH, therefore the yields determined in this work should be applicable to higher RH.”

What is the absolute detection limit for glyoxal for the averaging used in the determination of the time series? And the same comment for methylglyoxal. What is the lifetime

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methylglyoxal method? What is the LOD for glycolaldehyde and hydroxyacetone? How much additional NO was added (compared with NO_x might be present with the HONO)

The detection limit for glyoxal is 2.9 ppt in 30 s (3 σ). 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 270 ppt in 5 minutes (3 σ) for glyoxal and methylglyoxal, respectively, are achieved with this method.

The LOD for glycolaldehyde and hydroxyacetone is not known, but is assumed to be below the levels of glycolaldehyde and hydroxyacetone seen in the experiments. The initial NO in each experiment is indicative of the additional NO added.

For the determination of [OH] from the decay of the 3 VOCs – were the OH values consistent for each VOC decay? There is an opportunity for 3 independent measurements of this parameter. What sort of smoothing was performed? Fig S1 the scatter in the OH looks OK, so why was the smoothing necessary? How sensitive are the results to any errors in the OH concentration?

While there was some difference between the values of OH from ISP, MVK, and MACR, the overall trend was similar. The VOC data were fit to an exponential or double exponential because slight increases in these values due to noise resulted in calculations of negative OH. This can be seen in Figure S2, which we are adding to show the effects of the smoothing on OH and the three different calculated values of OH.

What was the LOD for isoprene below which OH could no longer be determined from the isoprene decay?

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The LOD for isoprene is 0.5 ppb.

The methodology for determination of the first-generation yields is robust and should yield reliable values.

Did Dibble state an error for his calculations? Comparisons are made to these calculations and so this would be useful information.

No error is published in the study by Dibble, so we are unable to make comparisons.

Could a little more be said on why the methylglyoxal observations are inconclusive?

For experimental and instrumentation reasons, the methylglyoxal results were not conclusive for the isoprene experiments. However, the methylglyoxal signal in the MACR experiments was strong enough to analyze.

Page 10702 – line 18, could more be said about why the VOC and NO concentrations were not constrained to actual measurements, but predicted by a model just using the initial concentrations?

VOC and NO concentrations were not constrained to actual measurements in order to validate the model and ensure that the precursors as well as the higher generation products are well reproduced with the model. If measured and modeled concentrations of these species do not match, this could indicate a discrepancy in compounds such as OH, which would need to be investigated before the model could be fully validated.

If NO₂ was sometimes > 1000 ppb, this ought to be included in Table 1, which only shows NO, and this is quite a bit lower than this.

We have added a column in Table 1 showing initial NO₂ concentrations as well as a figure showing NO₂ during a typical experiment.

10703, line 13, MBO is not defined

Thank you for pointing that out. We have fixed this and added a definition.

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10705, line 21. Reason given is that OH is not measured, but is calculated from isoprene, MVK and MACR decay. Some more discussion then is needed about the error in OH from this method. How well did the OH concentration agree from the decay of the 3 hydrocarbons? Is the value used some average of the 3?

The agreement in OH calculation methods varies slightly between experiments, and the error in OH during the period where averaging was necessary will be shown in a new figure showing all species over the course of the experiment.

Could C₅ carbonyls be defined a little more precisely (or ref to a figure where their structure can be seen).

We have defined which C₅ carbonyls we are referring to from the MCM (HC4ACHO and HC4CCHO).

10707, line 8-9, areas dominated by isoprene... give a reference and perhaps the location. What is the NO_x at these locations?

This reference is not specific to one location, but to the fact that if models are over-expressing glyoxal from isoprene in chamber studies, there is a good chance they are also overpredicting glyoxal in areas dominated by isoprene.

Table 2. What is estimated HO₂ or RO₂ concentration in the chamber (from the model)?

Estimated HO₂ and RO₂ concentrations in the chamber varied with the concentration of precursor VOC, but were very similar to each other. They quickly rose and then fell from $\sim 5 \times 10^8$ molec/cm³ to $\sim 2 \times 10^8$ molec/cm³ by the end in the 2008 isoprene experiments and were approximately an order of magnitude lower in the 2009 and 2010 experiments. HO₂ concentrations in the MVK and MACR experiments started out at $\sim 2 \times 10^6$ molec/cm³, and were $\sim 0.5 \times 10^6$ molec/cm³ by the end of the experiment.

The equations on Fig 1 are quite complex, better in the text?

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We have changed how we explain this section and have moved the equations to the text.

Fig 4. Only one dotted line? What is solid red line?

We have added a second dotted line to indicate that glycolaldehyde yields from C5 carbonyls were also adjusted, and explained that the red line is a yield that was verified in this study and that of Chan et al. (2009).

Fig S1. Is this an average OH from the 3 decays of the 3 different VOCs? There is only 1 OH set of points.

In the first part of the experiment, the OH is only calculated from isoprene, but OH later in the experiment is an average of that calculated from isoprene, MVK, and MACR, and then of just MVK and MACR.

References

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Peeters, J., Nguyen, T. L., and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, *Phys Chem Chem Phys*, 11, 5935-5939, 10.1039/B908511d, 2009.

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