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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.

Anonymous Referee #3

Received and published: 1 June 2011

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 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 correla-

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tions 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 photolyse 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? 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?

Detailed comments.

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

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

The RH is quite low in the experiments - comment about not expecting the results to

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be sensitive to this parameter.

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 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)

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?

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

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.

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

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?

If NO₂ was sometimes > 1000 ppb, this ought to be included in Table 1, which only

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shows NO, and this is quite a bit lower than this.

10703, line 13, MBO is not defined

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?

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

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

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

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

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

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

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

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