

Interactive comment on “Rapid formation of isoprene photo-oxidation products observed in Amazonia” by T. Karl et al.

P. Wennberg (Referee)

wennberg@gps.caltech.edu

Received and published: 20 July 2009

Karl, Guenther, Turnipseed, Artaxo, and Martin present evidence from the field for the prompt formation of hydroxyacetone from the photooxidation of isoprene. The measurements are interesting but the analysis is too limited to warrant publication at this time. The manuscript is challenging to follow.

Major comments

1. The presentation of the vertical profiles and flux estimates (Sections 2.3 and 3.1) are tangential to the analysis and discussion and should be removed. These observations could form the basis of a separate paper.
2. The analysis approach considers a time trajectory in a box model with constant
C3090

isoprene supply. While this approach addresses one aspect of the time dependence, it does not address the issue of mixing. The distribution function of oxidative age is not simply due to the continual addition of isoprene but also reflects the mixing of aged air from aloft. While it may not be possible to directly model how this impacts the conclusions of this work, the importance of this mixing should be addressed via a sensitivity study.

3. The authors ascribe the rapid formation of hydroxyacetone to a first generation process involving the reaction of the isoprene peroxy radicals with NO. Paulot et al argued, however, that significant yields of hydroxyacetone arise quite promptly in the 2nd generation via the (very fast) reactions of the isoprene nitrates (ISOPN) and the hydroxycarbonyl (HC5) with OH. We suggest that the authors implement the Paulot et al. mechanism (Table 3, ACP, 9, 1479, 2009) to confirm that the hydroxyacetone concentrations they measure are not consistent with the 2nd generation yields from the ISOPNs and HC5.

4. The authors should discuss the recent paper of Peeters, Nguyen and Vereecken (Phys. Chem. Chem. Phys., 2009, 11, 5935 - 5939, DOI: 10.1039/b908511d). Although Peeters et al did not comment on the implications of their study for environments such as AMAZE-08 where the peroxy radical chemistry is dominated by NO but where NO is less than 10 ppb, the thermochemical stability of the isoprene peroxy radicals calculated by Peeters et al implies that the distribution of isomers will be determined by thermodynamics rather than kinetics. This in turn suggests that the 1,4 and 4,1 isomers will react with NO much less frequently than estimated from the laboratory experiments. Indeed for NO mixing ratio of 100-300 pptv (pg. 13636), the yield of 1,4 and 4,1 products would be nearly zero, while the sum of the yields of MVK and MACR would be ~90% with the remaining 10% being the 1,2 and 4,3 ISOPN. If true, this suggests that all the non-MACR routes to hydroxyacetone identified by Paulot et al would not occur in the AMAZE-08 environment.

5. The presentation of the material is not kind to the reader. It would be very helpful

to have the prose divided into more PP each with topic sentences to guide us through your data and analysis. Many PP go on for pages while containing many ideas and pointing to numerous figures. The section headings are misleading.

Technical Corrections

p13633 line 7: Moreover ... MVK + MAC : The authors suggest that glycolaldehyde/acetic acid are not correlated with either isoprene or MVK/MAC. This is somewhat surprising since Dibble et al. 2004 a,b and Paulot et al. suggest that the double hydrogen shift which results in the formation of hydroxyacetone in the delta 4,1 branch should yield glycolaldehyde and methylglyoxal from the delta 1,4 branch. This observation also is at odds with the mechanism used by the authors to suggest prompt formation of glycolaldehyde (Table 2). If the authors are certain that their measurement is representative of glycolaldehyde (and not acetic acid), this constitutes an important result which should be discussed. See also major comment 4 above.

p13638 line 24-29 The discussion of the chemical mechanism should be expanded along the following lines:

The authors do not refer to the proper work of Dibble (2004 a,b) to support the discussion of double hydrogen shift mechanism (these papers, contrary to the statements in the manuscript, did not suggest hydroxyacetone formation). We suggest the authors reproduce the double H transfer hypothesized by Dibble et al. to help the reader understand the proposed source of hydroxyacetone (4% yield) as described by Paulot et al.

Finally there is no mention of a double H transfer in the work of Paulot et al. with respect to the organic acids or organic nitrates. (line 28).

p13639 Section 3.3

The discussion of OH lifetime in the literature is very clouded and this manuscript could help clarify things by showing how sensitive the calculated OH lifetime is to assump-

C3092

tions about the general mechanism when many/most of the short-lived intermediates are not quantified. A case in point: If the major 'fast' source of hydroxyacetone is from the oxidation of ISOPN and HC5 (rather than the double-H transfer), this chemistry converts more reactive OVOC (HC5 and ISOPN) to less reactive OVOC (hydroxyacetone), in contrast to the claims made.

The use of Yiso for 3-MF is perhaps not sound. There have been contradictory reports on the source of methylfuran (from HC5 or from its parent hydrocarbon) so we suggest the authors use:

Yiso (HYAC+GLYALD+MeGLYO+GLYO) + (.45-Yiso)*alpha*3-MF+(.45-Yiso)*(1-alpha) HC5

Note that such a large yield for the delta channel is unrealistic and results from the absence of nitrates and the underestimation of MVK yield in the authors' scheme. Again, note major comment 4 above as these yields assume that the chamber study is representative of the much lower NO environment of AMAZE-08.

p13633 line 7: Moreover ... MVK + MAC

This sentence is very difficult to understand

a) Should "neither and nor" read "either and or"?

b) It is not clear how the absence of correlation between isoprene and MVK+MAC supports the identification of m/z 75 as hydroxyacetone

c) A correlation cannot correlate with another correlation. Do the authors mean that isoprene does not correlate with m/z 61?

p13634 Section 2.3

If this section is retained, more details should be given with respect to the gradient flux method.

C3093

p13635 Section 3.1

line 8 to 12 "The specificity ... in the past" belongs to section 2.2

p13637 Section 3.2

line 18 Evidence for the formation of hydroxyacetone from biomass burning requires a reference
line 19 the use of acetonitrile as a biomass marker needs a reference

p13638 line 7

It is somewhat unclear whether the authors actually took into account the photooxidation of hydroxyacetone as suggested by Table 1 and 2 or neglected it as suggested by equation (2). This should be clarified.

Fig 2

Fig 2 would be easier to understand if separated into two panels: a) MVK/MACR vs isoprene b) hydroxyacetone vs MVK/MACR

Fig 3a caption

Booth ? Both

Table 1

all the 10^a should read 10^{-a}

HC5 IUPAC name should be given what was assumed for HC5 fate ?

The authors should mention that the rate constant measured by Dillon et al (2006) is larger than the one commonly used (IUPAC states 3×10^{-12} a factor of two slower). This recent measurement was found to be consistent with the hydroxyacetone signal measured in chamber experiments (Paulot et al.)

Table 2

It should be stated in the caption that this mechanism only applies to high NOx

C3094