

Review of “OH and HO<sub>2</sub> radical chemistry during PROPHET 2008 and CABINEX 2009 – Part 1: Measurements and model comparison” by Griffith et al.

This paper describes laser induced fluorescence measurements of OH and HO<sub>1</sub>+ isoprene-based peroxy radicals during two field campaigns in a forested environment in northern Michigan. The measurements are compared with a constrained box model based on RACM chemistry modified to include the Mainz isoprene mechanism (MIM). Other recent mechanistic changes to isoprene oxidation (i.e. formation of epoxides and hydroperoxy aldehydes) were not considered in this paper, but are to be the topic of a future paper. The model tends to overpredict both quantities, but only slightly for OH even with 1-2 ppbv of isoprene present. This is in contrast to other recent observation-model comparisons (Lelieveld et al., 2008; Kubistin et al., 2010) in which models significantly underpredicted OH and HO<sub>2</sub>. Various theories to explain these latter measure-model differences have been put forward.

The measurements of HO<sub>x</sub> radicals are described in some detail as they relate to these studies. This includes important issues of background and interference in the conversion of HO<sub>2</sub> to OH by reaction with NO. Other supporting measurements needed for the box modeling are also described.

The paper presents data and analyses that contribute to the collection of HO<sub>x</sub> observations in forested environments and should be published. The authors may wish to consider minor comments below in the preparation of the final version.

Other comments.

Line 27, page 33168 to Line 2, page 33169. The sentence is worded in a way that seems to indicate the Kubistin et al and the Lelieveld et al papers are focused on different field studies, but in fact they are both using data from GABRIEL. Suggest a slight rewording.

Discussion of background, page 33172. Spectral interferences are discussed, but the recent reported issue of a difference between spectral background (off-line tuning) and chemical background (addition of an OH scavenger) is not discussed here (although mentioned at the bottom of page 33174, top of page 33175). I do see that it is discussed in detail on page 33183. Suggest at least a sentence or two here indicating the approach and that it will be discussed later.

Bottom of page 33172 to Top of page 33173. Would be worth a sentence to indicate what happens to RO<sub>2</sub> radicals (also discussed later – page 33175) when exposed to NO in the sampling cell.

Lines 20-25, page 33173. Detection limits are given, but how about overall uncertainties that include all of the terms associated with deriving a radical concentration (calibration, counting statistics, laser power measurement, etc.). This is important when comparing the measurements with the box model (for which you do describe uncertainties later). I see that it is mentioned in the Figure 5 caption, but a mention in the text would be good.

Discussion of peroxy radical “interference”, Page 33176 and supplement. Is it possible that the degree with which the FAGE instrument is sensitive to RO<sub>2</sub> depends on factors such as sampling cell pressure, time from NO addition to fluorescence measurement, NO concentration, or other factors? This could complicate the measure-model comparisons. Suggest at least briefly discussing the possibility. One item that would help the reader understand the importance of this issue is showing modeled HO<sub>2</sub> in Figure S5 (I do see that it is Figure 5). One could argue that the “interference” changes with time from 0 up to including all of the ISOP peroxy radical.

Discussion of model, page 33177. The model is well described. Has it been compared with other models? If measure-model ratios are to be discussed from different studies, and with different models (e.g. GABRIEL), then some connection between the studies is critical. The statements that

RO<sub>2</sub>+RO<sub>1</sub> chemistry may not be complete in RACM is of concern in this regard, although typically these reactions are not major loss routes for RO<sub>2</sub>.

Measure-model OH and HO<sub>1</sub>\* comparison, page 33180. It is not clear from the text or examination of Figure 5 that measured HO<sub>2</sub>\* is overpredicted by the model. It depends on whether you are comparing to modeled HO<sub>2</sub> or modeled HO<sub>2</sub> + ISOP (see earlier comment).

Lines 7-8, page 33181. You should indicate which way you are performing the linear regression (meas vs model or model vs meas). It is also known that standard least squares should not be used when determining the best fit for scattered x values. A bivariate fit is needed to get the proper fit parameters. Suggest doing the fits this way, unless you already have, in which case you should say so.

Figure 3 caption, page 33208. Suggest indicating in the caption that these are diel median profiles (i.e. versus time of day). Also indicate in the caption that PROPHET is blue and CABINEX is red.