

Interactive comment on “Measurements of tropospheric HO₂ and RO₂ by oxygen dilution modulation and chemical ionization mass spectrometry” by R. S. Hornbrook et al.

Anonymous Referee #2

Received and published: 23 November 2010

General Comments

This paper details the motivation, instrument development, laboratory parameterization, and application of a new technique for improving the measurement HO₂ and HO₂ + RO₂. The technical writing is superb and methodology of instrument development is well thought out. The paper has extensive detail on mechanistic chemistry, instrument design, calibration, and characterization, and only briefly presents an example of an atmospheric application, with little detail or conclusions, and refers to multiple future papers for the actual atmospheric science. Given that, I feel this paper more appropriate as an instrumentation/measurement development paper in a technical journal.

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From the ACP home page, "The journal scope is focused on studies with general implications for atmospheric science rather than investigations that are primarily of local or technical interest." There is the potential of interesting science from Figure 11 and 12; however, the results are not discussed in enough detail to make this paper appropriate for ACP.

In my opinion, this manuscript it would be well suited for submission to AMT and to leave only one atmospheric science example in this paper, probably Figure 10. Then Fig. 11 and 12 should be removed and used in one of the future papers.

If the authors insist on having the paper re-considered for ACP after revision, much more atmospheric science needs to be added. For example, a start would be plotting modeled versus measured HO₂/RO₂ colored by NO. This addition will enhance the scientific contribution of this paper by discussing measurement to model discrepancy with increasing NO_x as previously reported by Faloon et al., 2000, Ren et al., 2005, and 2006, etc.

A presentation of the intercomparison to the HO_x measurement in the DC-8 from INTEX-B is critical and will broaden the scope of this paper. What do these comparisons say about radical measurement techniques and what is the benefit the PerCIMS application?

Specific Comments

In Figure 12, a comparison to OH measurements (as opposed to only acetaldehyde), will be valuable for examination of model constraints. Using acetaldehyde model discrepancy is only justified if the author's measurements are used to better constrain the model. I suggest using the HO₂ and HO₂ + RO₂ measurements to further develop the model and present those results.

Schemes 1 & 2: Please revise these schemes to be more understandable, in particular explaining in the captions why pathways are bold, gray, etc.

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Figure 1: The manuscript refers to the 'neutral chemistry' and 'dilution' regions of the inlet but those regions aren't specified in the figure, add these labels.

Table 6: "RO₂ Measured?" as a column heading is misleading. This wording assumes the functional group is directly measured by the PeRCIMS.

Section 1, Introduction:

- Line 13 page 22221: "presently-available techniques ... do not provide speciated measurements of individual RO₂, but rather a sum of RO₂"... However, in this manuscript, the modified instrument can only separate out HO₂ and HO₂+RO₂, and cannot provide speciated RO₂.

- Line 3 page 22224: "... simultaneously provides better measurement sensitivity and separation than with dilution alone" there is no evidence (numbers) backing up this claim.

Section 3, Instrument Characterization

- Line 5-8 page 22237: How is the inlet pressure reduced to 100 torr? Pumping activated by a computer controlled sensor?

- Line 16-20 page 22240: "Overall, due to the differences in sensitivity of the PeRCIMS to different RO₂ radicals, reported measurements of ambient HO₂ +RO₂ and HO₂ must account for the relative reactivity of RO₂ precursors in the air masses being studied." Why and how? This claim is not justified without more discussion or a reference.

- Line 8 page 22242: "We found it not possible to explain our laboratory observations of the sensitivity of RO₂ radicals in our instrument." This is in conflict with the statement above (Line 16-20 page 22240)

Section 4, Measurement

- Line 17 page 22244: "The rate coefficients for RO+O₂ were set to their recommended values (1×10^{-14} for primary RO and 8×10^{-15} for secondary RO), and to zero for

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tertiary RO." Need reference.

- Line 5 page 22249: "Excluding data points with measured or modeled peroxy mixing ratios <2.5 pptV as well as those with corresponding 1-min average [NO] > 0.5 ppbV ..." What is the justification for excluding these observed ranges?

- Line 15 page 22249: "O-D photochemical models". I think this should be "0-D" (with a zero and not a capital "o"). The concept of 0-D was not defined in this paper. Either explain 0-D or revise sentence to say LaRC box model.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 22219, 2010.

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