Review of "Evaluation of OH and HO_2 concentrations and their budgets during photo-oxidation of 2-methyl-3-butene-2-ol (MBO) in the atmospheric simulation chamber SAPHIR" by Novelli et al.

This paper describes the data and analysis from a chamber experiment in which MBO was oxidized in the presence of NO_x. Measurements of HO_x radicals, oxides of nitrogen, ozone and organic compounds were made as functions of time during the experiment that included three additions of MBO spaced about two hours apart. The observations were compared with calculations using the Master Chemical Mechanism model modified to include hydrogen shift reactions of peroxy radicals. From the comparisons, it is concluded that oxidation of MBO is well-represented by MCM, and that observed levels of OH and HO_2 in two studies that exceeded calculated amounts cannot be explained by radical recycling in the oxidation of MBO.

General comments.

While the agreement between observations and the MCM model is impressive, this reviewer is concerned that a single experiment may not cover a sufficient range of conditions (e.g. NO, O_3 and MBO levels, j-values) to fully test the MCM MBO oxidation mechanism. Because of this, it is premature to conclude that MBO oxidation chemistry is fully understood. It is important to conduct experiments at very low NO levels, so that the other peroxy radical chemistry can compete with oxidation by NO. The background chamber chemistry, while having been characterized and discussed in the literature, is also of concern. Since the nature of the OH reactivity is not fully understood, one is left to wonder whether the specie(s) contributing are also impacting the types and chemistry of peroxy radicals produced in the chamber. A measurement of RO_2 would help clarify the radical chemistry. Also, presentation of attempts to model the background chemistry (that were not shown because of "the unknown chemical nature of the background reactivity") would give the reader an indication of its cause and behavior, obviously without repeating everything in previous papers on this topic.

This reviewer is willing to accept the paper (with revisions) based just on the one experiment, but the conclusions would be much stronger with additional chamber runs. Suggest the authors consider more experiments before publication.

Specific comments.

Abstract. In reading the first half of the abstract, this review was confused whether the discussion was related to the present study. Suggest adding something like "Several previous field studies" to indicate that this text is background information for the present study.

Page 1, line 17. Suggest "…studies have reported unexpectedly large…"

Page 1, line 18. Suggest "…mechanisms that largely…" or just eliminate "…which largely underestimated the observations", since unexpectedly large observations and model underestimations are essentially the same thing.

Page 1, line 22. Suggest "…radical concentrations showed…"

Page 1, line 28. Suggest "…trace gases agreed well…"

Page 1, line 30. Suggest "…cannot contribute in reconciling the unexplained…"

Page 2, line 17. Suggest "…radical concentrations measured…"

Page 2, line 40. Suggest "…within the Western US…"

Page 3, line 26. Suggest "…synthetic air until…"

Page 3, line 30. The statement about ozone duplicates what was stated in lines 27-28. Suggest consolidating.

Page 4, line 7. Suggest "…agreement between these two instruments…"

Page 4, lines 23-25. Is it possible to obtain concentrations of other hydrocarbon products that are expected (e.g. glycoaldehyde, HMPR, and others)? Also, do the PTR mass spectra offer any insight into

the missing OH reactivity? A statement as to why certain species are observed and others are not would be instructive for the reader.
Page 5. Line 9. This reviewer does not agree that agreement between measured and modeled concentrations cannot be expected during the initial phase (before MBO) addition. It is possible to constrain the nature of the OH reactant(s) by including a "CO-like" reactant and a "hydrocarbon-like" reactant. Suggest including the modeling results from the initial phase.
Page 5, line 30. Suggest "…more of the MBO that reacted…"
Page 5, line 35. Suggest "…although poorer than OH, was still satisfactory…"
Page 6, line 18. Suggest "…of any intermediates."
Page 6, line 28. Suggest "…missing OH sources, assuming the correctness…"
Page 7, line 1-2. Suggest removing "where y is the fraction of $O(^1D)$ reacting with water vapour multiplied with the OH yield of the $O(^1D) + H_2O$ reaction." This is given in page 6, lines 38-39.
Page 7, line 6. Suggest "…deviation becomes insignificant."
Page 7, line 18. Suggest "Here, different from the…"
Page 7, line 22. Suggest more description of what is meant by decomposition of alkoxy radicals, perhaps showing a sample reaction.
Page 7, line 26. Yes, the alkoxy radicals were not measured, but their abundance can be inferred from the rates of reaction of OH with hydrocarbons. This review suggests that a production of HO_2 can be calculated using steady-state assumptions for alkoxy radicals. Also, modeling exercises described earlier can help better constrain the background reactivity.
Page 7, line 36-37. Suggest "…when including the $L_{HO2,\ meas}$…"
Page 8, lines 1-20. When discussing BEARPEX and BEACHON-ROCS measure-model comparisons, it is important to identify whether the models used the same mechanisms as that used in this study. Suggest adding one or sentences to clarify this.
Page 8, line 32. Suggest "…state-of-the-art…"
Page 8, line 33-34. Suggest "…firstly, average observed to modeled ratios of 1.0 ± 0.2 and 0.9 ± 0.1 are found…"
Page 8, line 34-35. The observed to modeled MBO being near 1.0 does not mean the observed and modeled decays are in agreement. A fit of the ratios versus time for the observations and model would be better. Alternatively, a comparison of lifetimes for each of the decays could be instructive.
Page 8, line 38. Suggest "…do not have significant impacts on the model…"
Page 9, line 4. Suggest "…photo-oxidation as good agreement…"
Page 9, line 5. Suggest "As large discrepancies were also observed…"
Page 10. Suggest a note in the table to indicate that accuracy estimates are for concentrations well above the detection limit (which is three times the precision? Or ?). Also, suggest a note to indicate the PTR precision and accuracy values vary with compound. Could give a range of values rather than > and < values.
Page 15, References. Suggest using hanging paragraph indent, as it is difficult to find a specific reference with the current format.