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Atmospheric
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Interactive comment on "OH and HO_2 chemistry in clean marine air during SOAPEX-2" *by* R. Sommariva et al.

Anonymous Referee #2

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This manuscript describes modeling studies of the HO_x radical chemistry in the low-NO_x marine boundary layer in the Southern Ocean. The authors employ two models which are based on the Master Chemical Mechanism. One of the models is based only on CO and CH_4 chemistry to drive the HO_x cycle. The other additionally considers other hydrocarbons. Both models are constrained by observations taken during the SOAPEX-2 experiment which was held at the Cape Grim Station in Tasmania. The authors focus on days with NO_x levels below 15 ppt, addressing the radical chemistry in the clean air regime. To validate their models and the underlying chemical mechanisms the authors compare modeled values for OH and HO_2 with measurements by a LIF/FAGE instrument during this campaign. The comparison shows an excellent agreement between observed and modeled OH, in particular considering the limited accuracy of the OH measurements. The agreement for HO_2 is somewhat worse. However, considering the uncertainties in both observations and model, i.e. heterogeneous uptake of HO_2, the agreement is acceptable. An analysis of the reaction mechanisms reveals that HCHO plays an important role as an HO_2 precursor at the HCHO levels observed at Cape Grim. The source of HCHO is, however, unclear. The authors also suspect that, based on the poor performance of their model, uncertainties in the chemistry of HCHO remain.

The paper provides some interesting insights into the radical chemistry in clean air. It is well written and the methods employed by the authors are scientifically sound and well described. The authors should also be commended for providing a detailed sensitivity and uncertainty analysis of the models. It is rare to see an ”error analysis” for models, and one would hope that the methods applied in this paper will be used by other researchers. In summary, I believe that the paper makes valuable contribution to our understanding clean air radical chemistry and is thus worthy of publication in ACP. However, I would like the authors to consider a number of changes to the manuscript before final submission.

The authors use a number of field measurements to constrain their model and to compare them with the model results. While the uncertainties of many of these measurements are listed somewhere in the paper, it would be very helpful if they could be shown in one central place, for example by expanding Table 1. Consequently I would like to encourage the authors to include these uncertainties in their comparison between measured and modeled OH and HO_2. It would be particularly helpful to include the errors of OH and HO_2 in figures 1 - 6 and 8. The uncertainty should also be included in the discussion of the comparison. An agreement of 20% for OH between a model and a measurement method with an accuracy not better than 40% is quite good. The question of measurement accuracy also applies to the discussion of HO_2 and HCHO, since both measurements seem to have inaccuracies of 50%.

Much of the manuscript is dedicated to the discussion of the role of HCHO as a major HO_2 source. However, the approach taken by the authors constrains the HCHO in the

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model by the observations. At one point in the manuscript it is mentioned that if HCHO is not constrained the model calculates 50% lower HCHO concentrations. It would be interesting to know how the OH and HO_2 levels change if HCHO is not constrained. In addition, the authors could consider what would happen if the measured HCHO concentration is indeed lower by the 50% inaccuracy that was mentioned for the HCHO measurement. This discussion would help in explaining how the conclusion that there are uncertainties in the chemical mechanism was reached.

At various points in the manuscript the possibility that halogen chemistry may have an influence on the chemistry in the clean boundary layer is mentioned. Chlorine chemistry is included in the model. However, the heterogeneous release from sea salt, which has been considered as a major source of Cl at many occasions, is not considered as a source. It is thus likely that Cl levels at Cape Grim are higher than those in the models. Oxidation of methane and other hydrocarbons could have an influence on the radical cycle and the formation of HCHO even at Cl atom concentration of 1-5 x 10^4 atoms / cm^3. There are also now various examples of measurements of BrO at levels of 1 - 2 ppt, and of IO at levels of 0.5 - 1 ppt in the marine boundary layer. While I agree with the authors that an accurate quantification of halogen chemistry is difficult, it is important to discuss the possibility that part of the HO_2 discrepancy is due to halogen chemistry.

Minor/Technical Comments:

Page 428 line 20: ”..an aerosol..” should be ”..on aerosol”

Page 431 line 7 8: The authors should explain how OH concentration of 10^5 molec / cm^3 could be observed if the detection limit is 1.4 x 10^5 molec / cm^3.

Page 434 line 2: Should ”propagation/termination rates” be ”propagation/termination ratios” ?

Page 441 line 20: ”NO < 4 ppt” instead of ”NO < 3 ppt”

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 419, 2004.