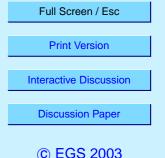**Atmospheric Chemistry and Physics Discussions**

Interactive comment on "Hohenpeissenberg Photochemical Experiment (HOPE 2000): Measurements and photostationary state calculations of OH and peroxy radicals" *by* G. M. Handisides et al.

Anonymous Referee #2

General comments:

This paper presents new results of OH and peroxy radical measurements performed at Hohenpeissenberg on four clear days in early summer. Their daytime and nighttime concentration levels are compared with the ones calculated within a simple model on the basis of the standard tropospheric chemistry mechanism by constraining the concentrations of radical precursors to observations. Reasonable agreement is achieved for both OH and peroxy radicals, although the difference between them is significant during certain time periods. In recent years radical measurements became available at many sites to be compared with the predicted concentrations. However, we still cannot

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tell systematically under which situations the prediction is not good or our current understanding of tropospheric chemistry is poor. In this sense much more measurements of radicals under various conditions are now desired. I believe that the measurements at Hohenpeissenberg, especially those for OH, have been carefully performed. I recommend that the observational results should be published in ACP as they appear in the manuscript. As compared to the careful measurements, however, I do not think that the performance of the calculation is sound in two points. First, the steady state assumption would not be satisfied throughout the calculations. The total production and loss rates for OH and ROx are first assumed to be equal to produce steady states (equation 15 in page 2520). However, the results (Figures 8 and 10, Tables 4 and 5) show that their total rates are not balanced. Sometimes the difference between them is more than 100%, showing clear deviation from steady states. I would doubt that the calculation is adequately performed and request revised calculations. Secondly, the authors assume that the HO2/RO2 ratio is 1 or 2 in the calculations. Actually, the ratio seems to fall within the range 1-2 as suggested from past studies. However, it can rather be predicted by the model itself and needs not to be assumed. For example, if ROx is divided into HO2 and RO2 and steady state assumption is applied to both species, we obtain three non-linear equations for three short-lived species (OH, HO2, and RO2). Using a numerical iterative method such as Newton-Raphson method, we can solve the simultaneous equations for the three unknown parameters ([OH], [HO2], and [RO2]), from which the HO2/RO2 ratio is determined automatically. This approach has been utilized in past studies (e.g. Cantrell et al., JGR 1996; Savage et al., Atmos. Environ., 2001), and would be a better way to predict HO2 and RO2 simultaneously at steady states. Only after revising the two points above, the model results are convincing to be compared with observations.

Specific comments:

1. page 2508, the last line The authors use "ROx" to define the sum of RO2 and HO2 (or total peroxy radicals), excluding OH and RO from "ROx". Usually the "x"

indicates the number of oxygen atoms (x=1 or 2) and includes OH and RO. In the troposphere, the OH and RO are far less abundant than the peroxy radicals unless NOx concentrations are extremely high, and therefore including OH and RO does not produce any significant difference in ROx. I would suggest that using either "total peroxy radicals (HO2+RO2)" or "ROx" including OH and RO is better than the definition used in this manuscript. Actually, the authors themselves make confusion in page 2521 saying that "the contribution of OH to the measured ROx concentration is negligible". A thorough definition is need.

2. page 2510, line 16-18. The authors only include references from three research groups out of five that achieved LIF detection of tropospheric OH and HO2. Publications from other two groups should be cited here (Holland et al., JAC, 1998; Kanaya et al. JAC, 2001) to make a more comprehensive reference list.

3. page 2510, line 18-21. During MLOPEX2 field campaign OH and ROx were simultaneously measured. Additional reference is required here (e.g. Cantrell et al., JGR 1996).

4. page 2510, last line - page 2511, line 1. McKeen et al. (1997) do not suggest that the observed mixing ratio of b-pinene fully diminishes the discrepancy between observation and calculation. Table 3 of their paper indicates that the discrepancy is removed only when b-pinene whose mixing ratio is higher than observed by more than a factor of 5 is assumed.

5. page 2511, line 18-19. "This allowed the model to be constrained by measured radical concentrations" The model is not constrained by "radical concentrations" themselves but by measured radical precursor or sink-partner concentrations. Please rewrite.

6. page 2512, line 16. The inlets for all trace gas monitoring instruments were located in "close" proximity to each other. How close were they? Especially the distance between the inlet for the radical instruments and that for the NOx instrument is important

to confirm that both instruments always sampled the same air mass.

7. page 2513, line 11-12. Maybe not "photocathode" but "photomultiplier" or "photodiode".

8. page 2514, line 2-3. What reacts with CO is not peroxy radical but OH that is produced by the reactions of peroxy radicals with NO. Please rewrite.

9. page 2514, line 16-24. The authors assume that the sensitivity of their PERCA instrument has the same dependence on the water vapor mixing ratio as that reported by Mihele and Hastie. However, it is likely that the dependence is different if the tube's diameter, length, or the gas flow speed is different. Have the authors compared these parameters with those of Mihele and Hastie's to reasonably assume that the dependence is the same?

10. Somewhere in section 2, the authors should include more information about NOx measurements. The detection limits for NO and NO2 should be included. Did the J(NO2) and J(O1D) measurements cover 2-pi or 4-pi sr solid angle?

11. section 3. All the time series data are given with CET. When is the actual local noon at the site?

12. page 2519, line 9. The term "OH oxidation rate" is not commonly accepted, needing definition. I suggest its definition (Sigma(i) {k(i) x NMHC(i) x [OH]}?) should be included.

13. page 2519, line 23-24. Do the authors believe that the peroxy radicals produced via the reactions of NO3 with alkenes (b-nitrooxy-peroxy radicals) are detected by their PERCA instrument? Certain types of the b-nitrooxy-peroxy radicals may not produce any peroxy radicals upon their reactions with NO due to thermal decomposition of the corresponding alkoxy radicals, preventing radical amplification (e.g. Ashbourn et al., JAC 29, 233-266, 1998). More discussion is needed here.

14. section 4. More discussion is needed for the uncertainties of the OH and ROx levels

calculated by the model. The most sophisticated way to predict them is the Monte-Carlo approach used by Thompson and Stewart (JGR 1991) and Carslaw et al. (JGR 1999). In the isoprene rich air mass, Kanaya et al. (JGR 2001) reported the uncertainty of OH was sometimes as high as 50-80%. Are the differences between observed and calculated radical concentrations really significant even when the model's uncertainties are adequately considered?

15. page 2521, line 10-13. Here an additional assumption in the MODEL (not measurement) is described and the equation (16) should be [HO2]model = [RO2]model = 0.5 [ROx]model.

16. page 2521, last paragraph. In the discussion of nighttime chemistry, the authors should include the calculated concentration levels of NO3.

17. page 2523, line 15-. The overprediction of OH concentration by the model is discussed. The authors focus on the data at 1100 CET, when rapid NOx changes might have influenced the HOx concentrations. I would recommend that the OH uncertainty range is calculated with the observed NOx concentration range during this time period, before concluding that the calculated OH concentration is significantly higher than that observed. Since the NOx abundance has a non-linear effect on OH and HO2 concentrations, it is not obvious that "this should only affect the variability in the calculated concentrations, and cannot explain the systematic overestimate of the OH concentration by the model (page 2524, lines 1-3)".

18. page 2524, line 14-15. As mentioned above, the authors should include the NO detection limit, which is used as its nighttime mixing ratio in the model. If it is so high as 15 pptv (as shown as its accuracy in Table 1), the HO2/RO2 ratio consistent with that amount of NO in the model can be as high as 1/2 because NO promotes production of HO2 by reacting with RO2 (e.g. Kanaya et al., GRL 1999), although the ratio of 1:1 would be an extreme assumption. If nighttime NO assumed here is several pptv, it may be appropriate that the HO2/RO2 ratio is well below unity, supporting the discussion

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given by the authors.

19. page 2524, line 16-22. The authors have to state why the total production and loss rates of OH given in Figure 8 and Table 4 are not balanced so often, as I pointed out in general comments. (Same for ROx in Figure 10 and Table 5.)

20. page 2526, line 21. "the reaction of ROx with O3" should be the reaction of HO2 with O3.

21. page 2527, lines 4-. The sentence starting from line 7, "However, as shown Ąc." is not clear. Perhaps "Thus it is likely that the nighttime production of ROx by the NO3 radical cannot be ignored for the conditions prevailing during HOPE 2000." is better.

22. page 2528, line 3. A typo is found. "net"

23. In the model, a constant level (3 ppbv) of formaldehyde is assumed. However, it is likely that the HCHO mixing ratio has a significant diurnal variation with a maximum in daytime. Can the authors discuss its effect on the estimated radical concentrations?

24. In the H2O2 and ROOH concentrations shown in Figure 2, we see regular variation patterns with a cycle of 1-2 hours. Are they real variations in peroxide concentrations or attributed to instrumental errors?

25. I suppose that Table 2 is incomplete. HO2 will not be produced from the reaction 4. For the reactions 15a and 15b, HO2 should be produced from the subsequent rapid reactions of RO or CH3O with oxygen. For reactions 16 and 16a, is it true that ROOR or CH3OOCH3 is produced with a yield of unity?

26. In Figure 3, the unit for jO1D should not be "molecule s-1" but "s-1". The unit for jNO2 should be included.

27. In Figure 11, two values from Scenario I resulted in negative values of ROx concentrations. What is the reason for this?

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 2507, 2002.