

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

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General Comments

The authors wish to thank the reviewer for his/her comments. They indicate some areas that needed clarification and have helped us (we hope) to improve the paper. We will respond to each of the points in detail below.

The first objection made by the reviewer to the model results presented in this paper relates to the assumption of steady state conditions assumed in the model. The objection appear to be based on a misunderstanding of the production and loss rates for the hydroxy radical (OH) and the peroxy radicals (RO_x) presented in Figures 9 and 11,

respectively. The production and loss rates presented in the paper are calculated using the **measured** OH concentrations and RO_x mixing ratios, and not those calculated using the steady state calculations. In contrast, the calculated radical concentrations were calculated by setting the production and loss rates equal, and solving the resulting balance equation for the concentration of the radical under consideration. The radical concentrations were not calculated simultaneously using numerical techniques, which appears to be the reviewers assumption. Instead the concentration of each of the radicals was calculated independently, using the measured concentration of the "other" radical as an input. Thus, the OH concentration was calculated using the balance equation and the measured RO_x concentration, and the RO_x concentration was similarly calculated using the measured OH concentration. In this way the calculated concentration of each radical was constrained by the measured concentration of the "other" radical.

Deviations between the calculated total production and loss rates shown in Figures 9 and 11 do not necessarily indicate that steady state conditions were not applicable, rather, as argued in the paper, they suggest that the simple photochemistry used in the model is not complete. This may be due to the assumptions made in the model, the accuracy of the measurements, or the fact that the set of trace gases measured during HOPE 2000 was incomplete. Any of these factors, or a combination of them, will result in the observed deviation between production and loss rates, and consequently to the observed deviation between calculated and measured radical concentrations.

The second objection to the model results pertains to the partitioning between the hydroperoxy radical (HO₂) and the organic peroxy radicals (RO₂). The reviewer suggests establishing a set of nonlinear simultaneous equations for OH, HO₂ and RO₂, and solving these "using a numerical iterative method such as the Newton-Raphson method", as used by [Cantrell et al.(1996)] and [Savage et al.(2001)]. In both the papers cited by the reviewer, the isoprene concentration was sufficiently low that the oxidation of isoprene could be effectively ignored, and the assumption was made that the hydrocarbon

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chemistry could be approximated by using “equivalent methane”. [Savage et al.(2001)] state that treating each of the peroxy radicals separately would increase the complexity considerably and is a major source of error in this approach. Under the conditions encountered during HOPE 2000, isoprene and biogenic hydrocarbon chemistry is found to be a major source of peroxy radicals. The chemistry of organic peroxy radicals produced from the oxidation of isoprene and monoterpenes is not well known and an appropriate description would require detailed information and complex modelling which is beyond the scope of this simple model. The assumption that methane chemistry is an appropriate description of the system would consequently introduce further errors into the model. Thus, the simplifications required to solve the system of equations obtained using the approach suggested here would only introduce further errors, and this does not seem justified in light of the other uncertainties discussed in the paper.

The text has been reworded in some places to clarify our procedure.

Specific comments

1. The definition of RO_X has been changed in the introduction to include both OH and RO radicals, i.e.: $RO_X = OH + RO + HO_2 + RO_2$. However, the concentration of OH and RO is sufficiently low that they can effectively be ignored. Thus, RO_X will be used to refer to both measured RO_X and calculated RO_2^* ($RO_2^* = HO_2 + RO_2$). Comments to that effect have been added to the text.

2. The suggested references have been added.

3. The suggested reference has been added.

4. There is no real contradiction between the paper by [McKeen et al.(1997)] and our paper. [McKeen et al.(1997)] show that the assumption of β -pinene concentrations 5 times higher than those actually observed result in better agreement between modelled and observed OH concentrations, but worse agreement for the peroxy radicals. Our paper refers simply to “Proxy assumptions for hydrocarbons with reactivities and

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mixing ratios similar to β -pinene led to an improvement ...", which interprets the effect of adding β -pinene to the system in terms of a hydrocarbon proxy. The text has been changed slightly to clarify matters.

5. This appears to be a basic misunderstanding of our approach which has been commented on above. A sentence has been added to the description of the model to try to avoid this misconception.

6. The maximum distance between the inlets of all trace gas monitoring instruments (including OH, NO_x, RO_x and VOC) was 7 m. This has been added to the text. The inlets of all instruments were positioned at the same vertical level (9-12 m above ground).

7. "Photocathodes" was changed to "phototubes", which is the term used by the manufacturer (Hamamatsu Inc.).

8. The sentence has been rephrased.

9. The parameters are similar to those of [Mihele and Hastie(2000)], whose instrument also uses 1/4" Teflon tubing. Unpublished measurements made at the Max Planck Institute for Chemistry in Mainz (Thomas Klüpfel, personal communication) using a Teflon inlet showed a nearly identical response of the chemical amplification factor with respect to water to that observed by [Mihele and Hastie(2000)]. The experimental method for determining the response of the amplification factor to water vapour was also identical. Further investigations using a different experimental technique and with an inlet made from plexiglass by [Reichert(2000)] at the University of Bremen confirmed the sensitivity of the inlet to water but the chemical amplification of this inlet dropped off more quickly with increasing water vapour concentration than any of the investigations using Teflon inlets. Due to the high degree of agreement between the two studies using a Teflon inlet, the sensitivity of the amplification factor towards water vapour was assumed to be identical to the chemical amplifier used by [Mihele and Hastie(2000)]. The interpretation of the various studies was complicated by the fact that [Reichert(2000)] used a different material for the inlet, and a differ-

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ent experimental technique for varying the peroxy radical concentration to measure the water effect. [Mihele and Hastie(2000)] varied the peroxy radical concentration by diluting the peroxy radical containing air used to calibrate the inlet with clean, moist air, whereas [Reichert(2000)] varied the production rate of HO₂ by adjusting the intensity of the UV radiation used to produce the HO₂ radicals. A paper published by [Reichert et al.(2003)] during the revision of the current manuscript indicates that the water effect is not solely due to wall loss, and suggests that the effect is due to reactions involving water complexes and CO or NO. A model was used to reproduce the measurements performed at the Institute of Physics in Bremen by Reichert and also those of [Mihele and Hastie(1998)]. The model results help to validate the data of [Mihele and Hastie(2000)] for a chemical amplifier with similar inlet parameters. Further studies are definitely required to characterise the effect of moisture more accurately and to determine its cause, and further measurements using the chemical amplifier most definitely require the water dependency to be determined directly.

A brief discussion of this effect has been added to the text.

10. Additional details about the photolysis rate and NO_x measurements have been added to Section 2.

11. A reference to time of local noon has been added to the site description and a further reference to true local time in the discussion of the OH concentration.

12. We have followed the reviewer's suggestion.

13. As pointed out by the reviewer, not all peroxy radical products of NO₃ radical oxidation are detected by the peroxy radical chemical amplifier, however this is not assumed in the paper. Model studies by [Ashbourn et al.(1998)] for rural England indicate that 70-80% of ambient nighttime peroxy radicals would be detected by a chemical amplifier. Under the conditions observed during HOPE we would expect a significant proportion of the peroxy radicals produced by NO₃ oxidation to be detected by the chemical amplifier, although this has not been tested. Additional causes of nighttime

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peroxy radicals are expected to be (1) the oxidation of alkenes by ozone, and (2) the persistence of organic peroxy radicals at low NO concentrations. HO₂ radicals are removed relatively rapidly due to reactions with other peroxy radicals, whereas the loss rates for organic peroxy radicals are slow enough to allow small amounts to persist [Monks et al.(1996)]. The contribution of ozone reactions have been included in the model, however no attempt has been made to model the persistence of organic peroxy radicals in this paper. While it is not expected that all the peroxy radical products of nitrate oxidation of biogenic alkenes will be detected by the chemical amplifier, the discussion in Section 4.4 indicates that the nighttime concentrations cannot be explained by ozone reactions alone, whereas the inclusion of nitrate chemistry results in a much better estimate of the observed concentrations.

14. The errors of the calculated OH and RO_x radical concentrations have been addressed in more detail. However, using a Monte Carlo approach as suggested by reviewer 2 appears inappropriate to solve this problem, since we are only dealing with simple uncoupled balance equations for which Gaussian error propagation is an appropriate method. The largest error contributions are due to (a) uncertainties in the measured radical concentrations, (b) the unknown concentrations of further VOC not measured here, especially oxygenated VOC, and (c) the speciation and chemistry of the peroxy radicals resulting from the oxidation of the VOC. Consequently, the uncertainties given in the paper are only rough estimates and depend on the assumptions made. When combined, they can add up to values exceeding 50%. An additional paragraph has been added to the text. Further discussion can be found at the end of Section 4.4.

15. This is indeed the case for calculated RO_x. However, in the case of the OH calculations, the measured RO_x concentration used to calculate the concentration of OH is assumed to be partitioned equally between HO₂ and CH₃O₂. The subscripts in the equation have been changed to reflect this.

16. We are aware of the problems involved in estimating the concentration of NO₃ due

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to the complex balance between gas phase chemistry, thermal decomposition of N_2O_5 , and heterogeneous loss of N_2O_5 . Our intent was to calculate the upper limit of the turnover rates of hydrocarbons due to NO_3 oxidation by assuming that losses other than the reaction with hydrocarbons are negligible. This is discussed in more detail in the revised manuscript.

17. When the data of June 19 is considered in detail, the highest variability in NO and NO_2 is indeed observed in the morning, but has greatly diminished by 9:40 CET. The highest over-prediction of OH is observed at 10:00 and 11:00 CET, i.e. slightly after the period with the highest variability in the NO_x concentrations. The OH budget at these times is most sensitive towards the NO and RO_x concentrations, since the reaction between these two compounds makes the largest individual contribution to the OH budget (see Figure 8), with $d(\ln[\text{OH}])/d(\ln[\text{NO}]) = 90\%$. However, it is not clear why June 19 is different from the other days since the meteorological and chemical parameters were very similar. Consequently, this paragraph has been reworded.

18. The NO mixing ratio at night was reevaluated based on a longer integration period of 1 hour. As a result, the upper limit for the nighttime NO mixing ratio is now estimated to be 6 pptv (see also comment 10). The text has been changed slightly to reflect this.

19. The changes at the beginning of section 4 should make this clearer. Additional changes have been made in the discussion in section 4.2 to further clarify matters.

20. We followed the reviewer's suggestion.

21. We followed the reviewer's suggestion.

Responses to the remaining points and a complete bibliography for both parts are contained in Authors' Response Part 2.

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