

## ***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 #1**

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#### General Comments

I enjoyed reading this article very much. It is very clearly written with some interesting results. Although not complete in terms of species measured (e.g. HCHO, HO<sub>2</sub>), and the model used is not very explicit, nevertheless the study enables some very useful conclusions to be drawn.

The paper describes a photochemical study made in Southern Germany in 2000. OH and the sum of peroxy radicals were measured, together with their important sink and source species, and comparison was made with a model constrained by these mea-

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surements. The study presented is limited to four days during an intensive period in the campaign. The agreement is very good during these four days, apart from some periods. In fact the agreement is surprisingly good given the limitations of the model, and the absence of some important species (See below). The authors are aware of the shortcomings of the model, and also that some measurements are missing, and demonstrate the possible effect of different scenarios on the model agreement when the values of the missing species are changed in the model. The authors also present a rate of production analysis for OH and ROx.

The major conclusions are that in this environment, reaction with NMHC is the major loss for OH, and the major source of ROx. The major production of OH came from the HO<sub>2</sub>+NO reaction, and this reaction also was the largest sink for ROx. The OH concentration was found to be largest in the late morning, when NO tended to be a maximum, and ROx peaked in the afternoon when the NMHC peaked (and hence the ROx production rate).

Overall the paper show the chemistry at this site can be adequately represented by the simple chemical mechanism included in the mode. The model only uses CH<sub>3</sub>O<sub>2</sub>, there is no speciation of higher peroxy radicals. Also, HCHO (or any other other carbonyls) was not measured, and a 3ppbv constant value was assumed. Also, HO<sub>2</sub> was not measured, and so the model assumed a ratio of RO<sub>2</sub>:HO<sub>2</sub> of 1:1 although this ratio was varied in other scenarios. There were no NO<sub>3</sub> measurements and so the night-time chemistry could not be tested adequately. These assumptions/omissions are major ones, and thus the very good model/measurement agreement presented in the paper maybe somewhat fortuitous with some cancelling of errors. Various combinations of the chosen carbonyl proxy concentration, HO<sub>2</sub>/RO<sub>2</sub> ratio etc. could have produced any desired level of agreement. The authors conclude that a future study should include these measurements and this is fully supported by the referee.

More specific comments/suggestions.

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(1) Given the probable number of oxygenated hydrocarbons, and also HCHO, a measurement of the photolysis frequency of these compounds would be very beneficial, perhaps using a spectroradiometer, rather than just J(O1D) and J(NO2). This ought to be added to the measurements to be included in a future campaign (in conclusions).

(2) The ROx levels measured (up to 70 pptv in places) are quite high, some comment on this and comparison with other ROx measurements would be useful.

(3) In G. Salisbury, et al. Production of peroxy radicals at night via reactions of ozone and the nitrate radical in the marine boundary layer, J. Geophys. Res., 106, D12, 12,669–12,688 (2001), it is shown that the reaction of O3 with alkenes is the most important night-time source of peroxy radicals, rather than NO3 measurements. There were both HO2 (FAGE) and RO2 (PERCA measurements), together with NO3 measurements (DOAS). In the HOPE 2000 study the authors should perhaps not jump to the conclusion that NO3 is the dominant source of RO2 at night. In the absence of any NO3 measurements this cannot be justified. What is the value of NO at night? Are there any local sources to maintain a small concentration? Would this limit the NO3 concentrations that can be achieved?

(4) Models such as the Master Chemical Mechanism explicitly consider oxidation of hydrocarbons, and it has been shown, for example with isoprene, that the rate of loss of OH by the oxidation products of isoprene is larger than the rate of loss of OH by isoprene itself. Hence, the OH loss is probably significantly underestimated in the model used if the species only in Table 3 are considered.

(5) Did the authors consider any heterogeneous chemistry at all? For example, uptake of HO2 on aerosols? Also, the wind speeds were generally less than 4 m s<sup>-1</sup>? In any still conditions, is the uptake of species on surfaces of any buildings/containers etc. expected to be important? Sampling of scrubbed gases may also be a problem under these conditions. Was there any dependence of the model/measurement agreement with wind speed?

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(6) 1.6 m between addition points of CO/N<sub>2</sub> in the PERCA? This may be a typo, wasn't sure.

(7) The humidity correction of Mihele and Hastie was used for the PERCA. How unique is the humidity correction from one PERCA to another? Why was this factor not measured directly for the PERCA used in these experiments?

(8) Fig 2. If NO could be plotted on an expanded vertical scale it would be useful. Apart from spikes it is impossible to see what the general level of NO is.

(9) There were two GCs used, one for C<sub>2</sub>-C<sub>8</sub> and one for C<sub>5</sub>-C<sub>13</sub>. As an internal inter-comparison was the same species ever measured on both columns? This is possible for DMS usually and also isoprene. If the measurements are staggered between the GCs it also would provide a higher temporal resolution.

(10) As discussed in Lewis et al 2000 (Nature) it is normally expected that GCs may miss a significant part of the carbon loading due to problems with peak separation. Although an impressive number of NMHC species were measured in the campaign, it is likely that there are many others not measured, and no oxygenated species are listed at all. Some mention of this is probably warranted.

(11) Page 7, first column, it is assumed that NO<sub>3</sub> builds up after sunset. This is true if NO is very low, but the NO+NO<sub>3</sub> reaction may limit the concentration of NO<sub>3</sub>. Was the night-time NO low enough that this reaction does not represent a significant sink for NO<sub>3</sub>?

(12) How accurate is the STAR method to get photolysis frequencies? Was the rate for J(O<sub>1</sub>D) and J(NO<sub>2</sub>) for example to compare with experiments? Has the method been validated before against a spectroradiometer for J(H<sub>2</sub>O<sub>2</sub>)

(13) The model is very simple, considering the large number of NMHC species that are present. However, this point is made clear by the authors, and the effects of the assumption used is discussed. However, for a future study, it is suggested that a more

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detailed model is considered, for example, the MCM, that is available on the Web.

(14) The atmospheric lifetime of OH is listed as 0.5 seconds. Assuming that it is defined by the reciprocal of the first-order loss rate due to reaction with CO, CH<sub>4</sub>, NMHC, HCHO, NMHC etc., then I would have expected the lifetime to be less than 0.5 sec? I have not done the calculation, but was a little surprised that it was not shorter, perhaps worth checking.

(15) The chemical composition of the system was not adequately determined on 19 June of course model/measurement discrepancy always suggests this!

(16) The BERLIOZ study showed that the HO<sub>2</sub>/RO<sub>2</sub> ratio changes significantly on a day-to-day basis and during the same day. It is good therefore that Scenario II was run. An important conclusion is that the chemistry can only be probed in detail if there is some knowledge of the speciation of RO<sub>2</sub>.

(17) The reason why the OH model/measurement discrepancy was much worse for PROPHET compared to HOPE is interesting, and not resolved. Good justification for more measurements.

(18) The paper is very well referenced.

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

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