**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Comparisons of observed and modeled OH and HO$_2$ concentrations during the ambient measurement period of the HO$_x$Comp field campaign" *by* Y. Kanaya et al.

Y. Kanaya et al.

yugo@jamstec.go.jp

Received and published: 1 December 2011

We appreciate the comments given by Drs. Müller and Peeters after their careful reading of our manuscript.

1. The first comment is that the OH yield of m = 3 from the photolysis of HPALD is too high if the isoprene chemistry is active for only a short duration of 12 min. We agree that the yield depends on the photochemistry of PACALD. Our original expectation was that 12 min is almost comparable to the photolytical lifetime of PACALD, ~16.7 min,

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

calculated from a J(PACALD) value as high as 10**-3 s**-1 at overhead sun (Peeters and Müller, 2010), and that the photochemistry of PACALD should proceed to some degree within 12 min. That was the reason why we made simulations of upper and lower bound cases by employing either m = 3 (S1 run) or m = 1 (S2 run). Upon Drs. Müller and Peeters' comment, we performed an additional model run (called S2mod here) employing a more explicit reaction scheme:

HPALD + hν (+2 O2) –> OH + HO2 + PACALD (1)

PACALD + hν –> 2 OH + carbonyls (2)
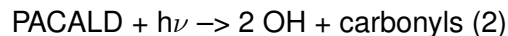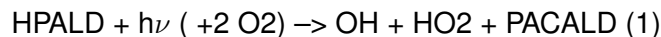
Here, HO2 is assumed to be produced from reaction (1) (following Peeters and Müller, 2010), not from (2) as suggested in the comment. The dependence of J(PACALD) on the solar zenith angle was assumed to be identical to that of J(HPALD). The OH and HO2 concentrations at around noontime in the S2mod run were actually between those simulated in the S1 and S2 runs; specifically the (S2mod-S2)/(S1-S2) ratio was about 0.2 for both OH and HO2. The results were slightly lower than our original expectation (the ratio would become about 0.5), where the degree of photodissociation of PACALD estimated from the photolytical lifetime (as mentioned earlier) was only considered. From the S2mod run results, we realized that the fact that PACALDs build up only gradually needs to be taken explicitly into account in addition. In the revised manuscript, we will mention the results of this model run and weaken the statement based on the S1 run. However, the original statement regarding the S2 run (lines 26-28 on page 28864) is still valid and our main conclusion is retained: "It should be noted that for OH and HO2 measurements by DWD, FRCGC, and FZJ, the slopes for the S2 run cannot be explained by the combined 1-sigma uncertainties of observations and model calculations."

2. The second comment is that the time period for which isoprene chemistry is active should be determined for the S-type model runs separately from the base run. We actually did this and the results were mentioned in lines 25-28 on page 28860 of the

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

original manuscript. To make it clearer, we will rephrase our statement in the revised manuscript as follows (see also our published author comment AC on our model approach): "... with isoprene oxidation durations of 10, 12, and 20min, the calculated MACR+MVK concentrations varied from 97% to 115% and 183% of observations as midday (09:00–15:00 UTC) averages over the three days for the chemical mechanism of the base run. Similar values (89 %, 107 %, and 175%, respectively) were achieved for the chemical mechanism of the S1 run. For best agreement, we employed 12min for the base and S1 run."

The concentrations of MACR+MVK calculated in the model pre-run made to determine the oxidation duration (12 min) with the S1 mechanism were actually lower (107% of observation) than those in the pre-run with the base mechanism (115% of observation), because of the lower yields of MACR and MVK as pointed out by the comment authors. However, the reduction of MACR+MVK in our S1 pre-run compared to the base case pre-run is only small. A possible reason is that our evaluation was made for midday (09:00-15:00 UTC) averages over the three days with different NOx levels. Actually, when the NO concentration was low at 12:30 UTC on 10 July, the MACR+MVK concentration in the S1 pre-run at 12 min was about 33% lower than that in the base case pre-run at 12 min. This suggests that the isoprene-active period should be determined from time to time. However, for HOxComp this optimization is limited by the sporadic MACR and MVK observations and their uncertainty. The impact of this limitation on the modeled HOx concentrations is small, because the isoprene oxidation time influences only the concentration of isoprene oxidation products other than MACR and MVK (the latter were constrained to observations in the actual base and S-type runs presented in the paper). For example, employing an oxidation time of 20 min instead of 12 min in the S1 pre-run at 12:30 UTC on 10 July increases MACR+MVK concentrations from 0.15 to 0.25 ppb, in better agreement with the interpolated observation value (0.28 ppb). However, the impact of using 20 min instead of 12 min in the S1 run was small; it increased OH and HO2 only slightly by 9% and 7%, respectively.

In our simulations with the S-type chemical mechanism, OH and HO2 concentrations rather increase (as stated above) when the isoprene-active time period is lengthened, contrary to the expectation by the comment authors. This is because the radical regeneration becomes more effective with a longer time. Therefore, increasing the isoprene-active time period in the S1 (and S2) runs rather increases the gap between model and observation.

The fact that the wind speed (2.6±0.7 m/s) and direction (355±17 degrees) were fairly stable for the midday (09:00-15:00 UTC) periods on the three days also allowed us to assume that isoprene chemistry was active for a constant period as a first approximation.

3. The third suggestion was to change the notation of ISOPEO2 and HALD5152. We agree that ISOPEO2 and HALD5152 represent different species in the two mechanisms. Different names will be used in the revised manuscript.

4. The last recommendation was to use a slower rate constant for the OH + NO2 + M reaction, which was newly determined with reduced uncertainty (Mollner et al., 2010). The new rate is within the uncertainty range (a factor of 1.3) of this reaction rate, which was taken into account in our Monte-Carlo analysis. A sensitivity model run employing the new rate actually yielded about 13% larger OH than the original run. It is within the uncertainty range of modeled OH as mentioned in the original manuscript. We will mention the impact of the new rate constant in the revised manuscript.

We thank Drs. Müller and Peeters for their comments helping us to improve our manuscript.

References

Mollner, A. K. et al. Science 330, 646–649, 2010.

Peeters, J. and Müller, J.-F. Phys. Chem. Chem. Phys. 12, 14227–14235, 2010.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 28851, 2011.

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper