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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign – Part 2: Model comparison and radical budget" *by* S. Dusanter et al.

Anonymous Referee #2

Received and published: 15 June 2009

Review of Atmos. Chem. Phys. Manuscript (# acpd-9-9823-2009) "Measurements of OH and HO2 concentrations during the MCMA-2006 field campaign – Part 2: Model comparison and radical budget" by Dusanter et al.

Scientific Significance: Good

Scientific Quality: Good

Presentation Quality: Excellent

1) Does the paper address relevant scientific questions within the scope of ACP? –Yes.

2) Does the paper present novel concepts, ideas, tools, or data? –Yes.

3) Are substantial conclusions reached? –Yes.

4) Are the scientific methods and assumptions valid and clearly outlined? –Yes, but see comments below.

5) Are the results sufficient to support the interpretations and conclusions? –Yes.

6) Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? –Yes, but see the comments below.

7) Do the authors give proper credit to related work and clearly indicate their own new/original contribution? –Yes.

8) Does the title clearly reflect the contents of the paper? –Yes.

9) Does the abstract provide a concise and complete summary? –Yes.

10) Is the overall presentation well structured and clear? –Yes.

11) Is the language fluent and precise? –Yes.

12) Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? –Yes.

13) Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? –Yes, but see special comments below.

14) Are the number and quality of references appropriate? –Yes.

15) Is the amount and quality of supplementary material appropriate? –Yes.

General comments

This is a companion manuscript of Dusanter et al. [2009] presenting the box model results for ROx (OH, HO2 and RO2) during the MILAGRO 2006 study conducted at a site in Mexico City. Field studies in polluted environments like this one are impor-

tant to test our understanding atmospheric photochemistry and oxidation processes. This study provides a relatively comprehensive (although limited VOC) measurement suite of important chemical species and physical parameters for model calculations to compare with the observations. The model results confirm the underpredictions of HO2 and HO2/OH ratios in high NO episodes, as found in some previous studies, suggesting that further investigation is needed in order to improve our understanding of atmospheric photochemistry. Photolysis of HONO and carbonyls was found the main radical sources while O3 photolysis was less important. In general the paper is well written and reports important results. My only concern is the large uncertainties in OH and HO2 measurements which make some conclusions not as strong as they could be (e.g., in Figure 5 the scatter of the measurement data points). I recommend it be published in ACP after revision, and ask the authors to consider the following comments in their revision.

Special Comments

P9828-9829, the description of LIF for OH and HO2 measurements and its calibration can be removed because they have been described in the companion paper (Dusanter et al., 2009).

P9832, L5, a factor of 1.04 was applied to reflect roof surface albedo. A brief explanation is needed (why 1.04).

P9833, bottom, the sentence “A reference VOC measured during both MCMA-2003 and 2006 exhibiting a similar rate constant with OH than an unmeasured VOC was selected to calculate the scaling factor.” is not clear to me. Which VOC species is selected as a reference VOC? Also, as the authors have stated that quite a lot of VOC species might not be measured in field studies, even with the combined suite of VOC measurements in both MCMA2003 and MCMA2006, it is possible that there are still missing VOC species (e.g., oxygenated species) which are not included in the model and may be partially responsible for the over-prediction of OH in the afternoon. The

author should include this possibility somewhere in the paper.

I noticed that the authors limited the comparison within the period between 8:40am and 6:40pm (CST). Any reasons for this? Were OH and HO2 only measured during this period? I am not sure when the morning rush hour is in Mexico City, but according to Shirley et al. (2006), the maximum NOx appeared between 5am and 8 am (CST) and apparently a period with richest chemistry is missing in this study. By the way, are there any nighttime OH and HO2 measurements?

P.9844, L.2, change “the measurements” to “the measurements of HO2”

P.9850, L.6-7, I would suggest adding “on average” or something like that when the authors state good agreement between observed and modeled HO2/OH ratios when NO was 1-5 ppb. The measured HO2/OH ratios are quite scatter as a function of NO while I assume the modeled HO2/OH ratios are much tighter.

P.9853, bottom, the authors pointed out the differences in the contribution of different ROx production processes. I wonder if the different locations (thus different chemical conditions) of MCMA2003 and MCMA 2006 could be partly the reason for these differences.

Figure 7, in the OH figure, the order of green-orange-red lines (from large to small) is consistent with the order of the additional HO2 production rates (i.e., green=2.2, orange=1.1 and red=0.7 x108 molecule cm-3 s-1). However in the HO2 figure, this order is red, green, and orange (from large to small). Is this an error?

In Figure 8, I noticed that there are at least two processes are not included in the termination: HO2+HO2 and HO2+RO2 to form peroxides (might be part of Figure 7, L(ROx) others). I also noticed that the total initiation rate and termination rate are slightly not in balance (e.g., P(ROx) = 11.4 + 5.7 + 2.8 + 11.7 =31.6 and L(ROx) = 6.5 + 4.6 + 19.7 = 30.8). Can these missing processes account for this discrepancy? Also the authors should mention that modeled RO2 (and modeled OH and HO2âĂŤI

assume) concentrations are used in the calculation, although other species are from measurements.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 9823, 2009.