Atmos. Chem. Phys. Discuss., 6, S3335–S3339, 2006
www.atmos-chem-phys-discuss.net/6/S3335/2006/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Night-time radical chemistry during the NAMBLEX campaign” *by* R. Sommariva et al.

Anonymous Referee #1

Received and published: 26 September 2006

General comments: Sommariva et al. investigate the nighttime chemistry of OH/HO2/RO2/NO3 radicals during the NAMBLEX campaign. Their analysis included comparisons between the observed and modeled radical concentrations and radical flux analyses in the model. Nighttime OH/HO2/RO2 chemistry and NO3 chemistry have been studied in various environments, but often they have been separately investigated because simultaneous measurements of all the radicals have been achieved rarely. It is new that the authors provide analysis with emphasis of the connections between the HOx and NO3 cycles, making full use of broad observations during the campaign. My major concern is that it is difficult to find out what is the original analysis of this paper in this special issue with many related papers (e.g. Smith et al. 2006, Fleming et al. 2006, Bitter et al. in preparation), which include nighttime analysis of

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

the radicals at least as their parts. This point needs clarification. Overall, this study is within the scope of Atmospheric Chemistry and Physics. I suggest that the paper should be published after taking into account the following minor comments.

Specific comments:

1.page 7717 last line: “especially”

2.page 7719, line 15. It is mentioned that the NMHCs data were linearly interpolated to 15 min. The original frequency of the NMHC measurements (40 min? from Heard et al. (2006)) should be included here.

3.page 7720, lines 10-19. It is not clear whether the observed boundary layer height is used in the model to calculated deposition rates.

4.page 7721, lines 2-4, 6, 11, and 15. Integration time and signal-to-noise ratio with which the detection limits of OH, HO2, HO2+RO2, and NO3 are calculated should be given.

5.In section 2, the times of sunset and sunrise should be specified for the campaign period to define nighttime.

6.page 7722, line 5. Nighttime OH was below the detection limit (6x10ˆ4 molecule cm-3). It seems from the inset graph of Figure 1a that modeled OH (fulloxy) sometimes reaches 1x10ˆ5 molecule cm-3. Does this suggest model’s overprediction of OH? Can the authors discuss nighttime OH levels with averaging intervals longer than 15 min?

7.page 7722, lines 9-10. Ěthe presence of an OH source unaccounted for or underestimated by the model “at sunrise”, such as HONO. How do the authors explain the model’s overestimation at sunset?

8.page 7722, line 17. Is the uncertainty of the model calculated for the nighttime of the NAMBLEX campaign?

9.page 7722, lines 26-28. Fleming et al. (2006) suggests that the peroxy radical increase with NOx is suggestive of NO3 reacting with hydrocarbons to form peroxy radical. However, this study shows that the increase in [HO2+RO2] with NOx increase is not reproduced by the model including NO3 chemistry. Are the model results completely different if constrained by observed NO3? Or is this positive correlation between NOx and HO2+RO2 attributable to unknown production of HO2+RO2 rather than NO3 chemistry? In Figure 1a and 1b, both observed HO2 and HO2+RO2 show peaks at around 22:00 - 23:00 when NO2 shows a maximum (Figure 7), while the modeled HO2 and HO2+RO2 do not show any peaks. These features could also suggest unknown production of HO2 or HO2+RO2.

10.page 7724, line 17. In Figure 3a, modeled NO3 is not shown. Only modeled NO3+N2O5 is compared to the measurement by CRDS.

11.page 7724, lines 20-22. How large is the uncertainty in the CRDS measurements of NO3? Can it be included in Figure 3a as error bars?

12.page 7725, line 17. Only effect on modeled [NO3+N2O5] (not [NO3]) can be seen in Figure 3a. Is heterogeneous loss of N2O5 with gamma = 0.016 - 0.032 slower than its gaseous reactions with H2O assumed in the model?

13.page 7726, line 2. Regina et al., 1998

14.page 7726. In addition to NO and DMS, can I2, measured up to 90 pptv in nighttime during the campaign, provide significant sink of NO3 by the reaction between them with a rate coefficient of 1.5x10ˆ-12 cm-3 molec-1 s-1 (Chambers et al. 1992)?

15.page 7726, last paragraph. Can a vertical gradient of NO, which is possibly present when considering its emission from soil, also affect the vertical NO3 gradient?

16.page 7727, line 25 and Figure 5. Are the two reactions OH + O3 and OH + H2 shown together in a single series in Figure 5?

17.page 7728, line 5. The authors mention that propene, c-2-butene, t-2-butene, c-2-pentene, and t-2-pentene are important to produce radicals from O3 + alkene reactions. In addition to propene concentrations specified in Table 2, the levels of the other alkene concentrations should be listed. The radical production rate from ozonolysis of propene is calculated to be only <2x10ˆ3 molecule cm-3 s-1, if using ozone and propene concentrations listed in Table 2, the rate coefficient 1.2x10ˆ-17 cm3 molec-1 s-1, and the OH yield of 0.33. This is only <20% of the decomposition rate of Criegee intermediates (1-2x10ˆ4 molecule cm-3 s-1) shown in Figure 5a, suggesting the importance of the other alkenes. Are the other alkenes emitted from anthropogenic activity? Is marine source important for propene?

18.page 7728, lines 17-18 and Figure 6a. It seems from Figure 6a that the main destruction of NO3 takes place by the NO3+NO reaction, not by the NO3+ NO2 reaction.

19.page 7729, lines 15-16. It is misleading to mention that NO2 was produced from NO, through its reactions with CH3O2 and HO2 and not to mention NO2 production from NO + O3 reaction.

20.page 7729, lines 25-27. The ozone decrease by about 30% (or by 10 ppb) cannot be fully attributed to the NO2 + O3 reaction. It is more likely that O3 is titrated by NO during the air mass travel from source region. The NO decrease is influenced by a larger degree by changes in emission and titration, rather than the change in the rate of NO3 + NO reaction.

21.Figure 8. The flux of the CH3O2 + NO reaction should be specified. It is questionable that the HO2 and HO2NO2 are not well balanced at 23:00 (with flux of +12.5), when NO2 concentration did not show a rapid change. Do the CH3SCH2O2 radical and other peroxy radicals produced from NO3 reactions produce HO2 by their reactions with NO? Is this more important “coupling” between NO3 and HOx chemistry rather than the shown ones?

22.page 7730, line 25. It is unclear to what HO2 and CH3O2 are important.

23.Fleming et al. (2005) all over the text should be replaced by Fleming et al. (2006)

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7715, 2006.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper