

Interactive comment on “Free radical modelling studies during the UK TORCH Campaign in summer 2003” by K. M. Emmerson et al.

Anonymous Referee #2

Received and published: 20 November 2006

This is generally an excellent manuscript, and I recommend publication. It presents a thorough comparison between measured OH, HO₂ and RO₂ radicals and 0-d model calculations, placed in context of previous studies. The results for the HO₂/OH ratio plotted versus NO, and the Q-Q plot, are especially noteworthy. These methods were used to identify model-measurement discrepancies that could easily have been overlooked. Other noteworthy features are the use of very detailed photochemistry (the MCM), the large impact of the HO₂-aerosol reaction and its sensitivity to the accommodation coefficient.

There is one possible problem with the scientific content - the treatment of PAN and related species and their impact on radical chemistry. There are also a number of minor comments and corrections.

Specific comment: Impact of PANs on radicals.

Results from Figure 8 show that formation of PANs from RO_2 (via $\text{CH}_3\text{CO}_3 + \text{NO}_2 \Rightarrow \text{PAN}$ and analogous reactions) is a major sink for radicals ($\text{OH} + \text{HO}_2 + \text{RO}_2$). This represents 20–25% of the total radical sink and is comparable in magnitude to the other two large sinks ($\text{OH} + \text{NO}_2 \Rightarrow \text{HNO}_3$ and $\text{HO}_2 + \text{aerosol}$). Presumably, this term represents net formation of PANs (i.e. the difference between production and PAN decomposition). In this type of calculation the net formation rate of PANs can be a model artifact, related to weaknesses in the 0-d calculation rather than to real net formation of PANs.

The TORCH experiment coincided with very warm temperatures, and the resulting lifetime of PAN with respect to thermal decomposition is approximately 30 minutes (day-time). In this situation the PAN concentration should be close to its steady-state value with respect to CH_3CO_3 . Several factors might cause PAN to deviate from its steady-state value, resulting in net conversion from radicals to PAN or vice-versus. An increase in O_3 with time would cause the steady-state PAN concentration to increase (due to the influence of the NO/NO_2 ratio on the PAN steady state), resulting in net formation of PAN. A decrease in VOC precursor concentrations would cause PAN to decrease. Circulation within the convective mixed layer might lead to net thermal decomposition of PAN at the surface, because air at higher elevations within the mixed layer has lower temperatures and consequently higher steady-state PAN.

The 0-d calculation used here does not include any of the above physical processes. Instead, net formation of PAN is based on calculated rates of formation from PAN precursors, which are derived or approximated from ambient measurements. (At least one major precursor, methyl glyoxal, is not measured directly.) Formation of PANs is complex and has many precursors, and any net imbalance between calculated sources and sinks is likely to represent imprecision in the calculation. The net imbalance between calculated PAN sources and sinks has the effect of introducing a source or sink for radicals. This net source or sink should be viewed as a possible model artifact.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

For this reason I believe it would be more accurate to set the PANs at steady state rather than to include net radical formation from PANs. Alternatively, net formation of PANs might be assumed to be proportional to the calculated increase in O_3 (based on calculations showing that steady-state PAN increases in proportion to ambient O_3).

I suggest the following changes in the manuscript:

(i) Add some discussion of PANs as a source of radicals in the manuscript, and address the above issues. At present, PANs appear in Figure 8 as a radical source, but are not discussed.

(ii) Consider showing results from an alternative calculation with PANs set at steady state. The current manuscript is worthy of publication without this addition, but it might be useful to show how results would change with this modification. (The same calculation would also illustrate the possible impact of the HO₂-aerosol reaction, which is similar in magnitude to PAN as a source of radicals.)

Other specific comments.

1. Effect of additional VOC: Although not necessary, the authors might consider adding results that show how an increase in total VOC would affect OH, HO₂ and RO₂.

Total VOC represents a significant uncertainty in the 0-d calculation. If the input to the calculation relied solely on measured VOC, then it would be biased towards under-representation (since measured VOC is never 100% complete). This study avoids this bias by adjusting input VOC's based on a trajectory calculation with emissions. However, this also introduces uncertainty based on the accuracy of the emission inventory.

This is important only because the model-measurement discrepancies for OH, HO₂ and RO₂ (underestimated RO₂, overestimated OH, slightly overestimated HO₂) suggest that the model underestimates total VOC, and that model-measurement agreement might be significantly improved if VOC were increased.

2. The analysis of radical chemistry in the text is presented in terms of sources and

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

sinks for summed radicals (OH , HO_2 and RO_2), including sources, radical propagation and termination reactions. This is clear to readers familiar with OH photochemistry, but the writing is sometimes confusing. The text refers to “sources of OH ” (e.g. p. 10525, line 21) and “ OH initiation” (e.g. p. 10537, line 23, p. 10544, line 1, and in the conclusion). This is confusing because the term “sources of OH ” usually refers to all direct sources of OH (including reactions viewed here as radical propagation). The term “ OH initiation” is also ambiguous. The writing could be made clearer.

The terms “initiation”, “propagation” and “termination” are introduced on p. 10537 and are clearly defined, but I suggest using a term such as “radical initiation via OH ” rather than “ OH initiation”. Also, the description in the introduction (beginning on p. 10525, line 20) is poor. The text begins with a discussion of “sources of OH ” and a subsequent discussion of radical sources, propagation and termination. Only the subsequent discussion makes it apparent that “sources of OH ” refers to radical sources through OH . Also, this discussion defines radicals as the sum $\text{OH}+\text{HO}_2$, whereas the rest of the paper defines radicals as $\text{OH}+\text{HO}_2+\text{RO}_2$. Please clarify the introductory paragraphs on p. 10525-6 so that readers will understand that you are referring to the sources of all radicals (preferably, $\text{OH}+\text{HO}_2+\text{RO}_2$) rather than OH .

3. The text refers to “PANs”, but does not define them or say how they are determined in the 0-d model. The text notes that PAN is measured. How are the higher PANs set? Are they set based on the trajectory model? If so, are they set in proportion to PAN? Please clarify.

4. The text refers to a radical sink via OH through PANs. I am not familiar with this. There is a $\text{PAN}+\text{OH}$ reaction, but its rate is normally very slow in the lower troposphere. It may be worth identifying these reactions in the text.

5. With regard to HO_2/OH : It may be worth discussing this in the context of results from Thornton *et al.*, 2002 (JGR). Thornton *et al.* argued for an OH source from isoprene (bypassing HO_2) in order to explain their measured HO_2 at low NO_x . The results here

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

suggest that the model HO_2/OH is overestimated versus measurements when NO is low (which may coincide with the conditions discussed by Thornton et al.) This appears to support the hypothesis of *Thornton et al.*

6. Please clarify in the text: Is the trajectory calculation used only to add secondary VOC (which were not included in the measurements but which are produced from measured VOC), or is the calculation also used to add primary VOC (which were not included in the measurements but which were believed to be present based on emission inventories)? The text (p. 10532) refers to the addition of species in proportion to benzene, o-xylene and acetone. This may refer only to primary species. The 0-d model almost certainly included unmeasured secondary species such as methyl glyoxal. Were these included based on the ratio with primary species such as o-xylene in the trajectory calculation, or were they set to steady-state values in the 0-d calculation? (It might be more reasonable to set them in proportion to measured secondary species such as acetaldehyde, but this is minor in context.) Please clarify how these species were set.

7. The text (p. 10532) includes the statement: “Consequently, there are model inputs for 84% of the primary emitted species in the model that are directly or indirectly based on measured values.” Please remove this sentence, which is probably a mistake. It raises a host of questions: Does this mean 84% of VOC based on the total number of species, or carbon content, or OH-reactivity? What are the other 16% of omitted species? (The text only described how unmeasured species were included indirectly and does not refer to species that were totally omitted.) Where does the 84% figure come from?

8. The introduction (p. 10526, line 13) states that the main sinks for HOx are the self- and cross-reactions of HO_2 and RO_2 and formation of HNO_3 . This is the “classical” understanding. However, this study concludes that aerosol reactions are the dominant HOx sink. The introductory summary here should probably also mention the aerosol reaction.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10523, 2006.

ACPD

6, S4746–S4751, 2006

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

S4751

EGU