**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Peroxy radicals in the summer free troposphere: seasonality and heterogeneous loss" *by* A. E. Parker et al.

A. E. Parker et al.

Received and published: 1 February 2009

Uncertainty: The authors should propagate measurement and rate coefficient uncertainties through equation 1 to provide readers with maximum allowed ranges in the parameters alpha, beta, and gamma. The authors do this to some degree when examining the impact of acetyl peroxy radicals on the inferred gamma.

Following the referee's request, we have performed a simple uncertainty sensitivity analysis viz

beta = LNOx/LSR

LNOx = ka[ROx][NO] LSR = kself[ROx][ROx]

Uncertainties can be estimated to be: ROx measurements 35%; NO measurements 5%; Rate constants ˜ 10%;

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Therefore uncertainty in beta = +/-40%

However, the effect on beta of changing alpha is as follows:

beta in "snow free" conditions: 9.22 when alpha = 0.25; 6.28 when alpha = 0.5; 5.20 when alpha = 0.75;

beta = ka[NO]/kself[ROx]

So now [ROx] * ka * [NO] * alpha / f* j(O1D) * O3

ROx uncertainty = 35%; ka uncertainty = ˜ 15%; j(O1D) uncertainty = 13%; f - ratio of rate constants = 10%; O3 uncertainty = 5%;

gamma error = ˜ +/- 42%

gamma in "snow free" conditions: 0.00682 when alpha = 0.25; 0.193 when alpha = 0.5; 0.358 when alpha = 0.75;

From the analysis the major uncertainty propagates from the value of alpha and the self-reaction rate constant.

For example, on page 17855, the authors state that measured HCHO yields a gamma term of 0.14, while the total gamma term is 0.19. Does this mean that the peroxy radical source term is closed to within 25%. Is the uncertainty in measured HCHO such that the dominant peroxy radical sources are explained to within the allowed uncertainty?

We have looked at this point and given, the HCHO measurement accuracy is 12% and j(HCHO) cross section + quantum yield +/- 13% max, spectral radiometer 9% with a maximum of 16%

The maximum uncertainty in the photolysis of HCHO = 20%

The following text has been added to clarify this point (see also reviewer 1 for H2O2 details)

"Furthermore, uncertainty in the measured HCHO is not sufficient to explain the re-

maining production. Ren et al., 2008 have reported that the photolysis of H2O2 can be a bigger contributor to HOx than HCHO at these altitudes. H2O2 was not measured during this campaign, however a concentration of 500 pptv H2O2 is sufficient to generate the remaining 0.05 of the total gamma. H2O2 measurements at the Jungfraujoch are scarce, but the mean H2O2 of 206 ś 261 pptv measured by Walker et al., 2006 during February and March 2003 suggests that this is not out of the question."

RO2 versus HO2: It seems like the authors have enough measurements to attempt to calculate the relative contribution of various species to RO2 by using the measured VOC, PAN, and NOx. This would be useful for ultimately determining the most appropriate rate coefficient for self reaction which in turn impacts the magnitude of peroxy radical loss unaccounted for by NOx and HO2+HO2.

Using OH reactivity as a guide (i.e. assuming that when an (O)VOC reacts with OH a peroxy radical is produced) and PAN decomposition, then acetaldehyde is the biggest NMHC contributor at about 10%. If you assume the reaction gives an acetylperoxy radical and then add acetylperoxy produced from PAN decomposition you have 12% of the "radical production", and around 60% of the non-CO, non-HCHO and non-CH4 "radical production".

We have already shown in the paper that even with 50% of RO2 as acetylperoxy that missing losses remain, so whilst the "real" self-reaction rate is likely to be somewhat faster than that calculated from HO2 and CH3O2 alone it cannot explain away the difference. For example, if we have 10% acetylperoxy, 40% CH3O2 and 50% HO2 then the self-reaction rate constant is some 20% faster than without acetyl peroxy. This remains an upper limit as it assumes that a) all OH loss VOCs have been measured, b) when we react acetaldehyde with OH one acetylperoxy is produced and nothing else e.g. HO2 and c) that there are no slower self-reacting peroxy radicals than CH3O2 present.

Terms in LNOx: The authors should explicitly state what reactions are contained in the

LNOx term. Is it just HO2 + NO and RO2 + NO? What about HO2+NO2-> HO2NO2 and CH3O2+NO2 -> CH3O2NO2? I would think these processes could be important under high NOx/cold conditions similar to the snowy days discussed at great length.

LNOx consists of OH + NO2, HO2 + NO and RO2 + NO

On the face of it HO2 + NO2 and CH3O2 + NO2 could make a significant difference but the rate of decomposition of the nitrates is about 2 and a half orders of magnitude faster than the rate of reaction of ROxNO2 with OH * [OH] making them an insignificant NOx loss process.

Physicality of khet: Can the authors determine whether the magnitude of the inferred heterogeneous rate coefficient is at all reasonable? For example, take typical snow grain number densities and size, together with diffusion-limited transport estimates under the assumption of unit accommodation/reaction and calculate a maximum heterogeneous loss coefficient. If the observed coefficient is larger than this estimate, it is likely gas-phase processes are missing.

At the time of writing the paper, the same calculation occurred to us. We concluded that a calculation would be very difficult to do as estimates of the parameters involved vary so widely

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17841, 2008.