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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 24 November 2008

This manuscript describes observations of peroxy radicals obtained at the Jungfraujoch, a site which almost certainly receives free tropospheric air. The peroxy radicals were measured by the chemical amplifier approach together with a number of other species important to describing peroxy radical abundance (VOC, NOx, PAN, HCHO, O3,etc).

The manuscript is well written and presents a comprehensive a data set that will be useful and of interest to ACP readers. I therefore recommend publication in ACP after some comments are considered by the authors related to their analysis.

Most of my comments are centered around issues related to equation 1.

Uncertainty:

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Interactive Discussion

Discussion Paper

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.

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?

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.

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.

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.

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Interactive Comment

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

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