This paper reports measurements of the solubility and first-order reaction rates of propionyl peroxynitrate (PPN) in water and n-octanol, and limited measurements of the solubility of acetyl peroxynitrate (PAN) in water. The data were then used to estimate atmospheric lifetimes of PPN against heterogeneous uptake in a number of scenarios. The measurements are solid and were well explained. I have only a few minor comments that need to be addressed and the paper should be acceptable for publication.

Line 45. It is not possible to make a blanket statement that the OH rate constants of PANs are low since MPAN (methacrylyl peroxynitrate) and APAN (acryloyl peroxynitrate) have unsaturated R- groups and are known or estimated to react rapidly with OH (Orlando and Tyndall, 2002; Orlando et al., 2002). The statement is true for PAN and PPN, but would benefit from having a range of lifetimes mentioned here.

Line 138. The mixing ratios noted here are quite high. Do they refer to the mixing ratios at the exit of the sources, or the entrance of the reactor. Most GC/ECD systems are limited in linearity at the high end. The technique used in this work relies on the detection scheme being linear with concentration over the range used in the experiment. How do you know your GC systems were linear at the highest mixing ratios used?

Line 155. The same idea as above, you need to justify the assumption of linearity.
Line 180. Instead of the word “known” here, the word “estimated” seems more appropriate.

Line 189. Was it possible to estimate $H$ and $k$ for ethyl nitrate? It looks like there is plenty of signal/noise for that peak.

Line 208 and Figure 5. The authors show, but do not explain points from Raventos-Duran et al., which appear to be estimates from structure-additivity relationships? This needs to be explained in the text.

Line 244. The Tables show lifetimes of 5 and 9 days, which are more than “several days”

Line 259. It would be useful to have the Kames and Schurath number for 278.15K in the table so we can see for ourselves.

Line 299. I think the authors mean “lipophobic” not “lipophilic”. Lipophilic fragments would tend to react with n-octanol.

Lines 312-314. There is a difference in PAN and PPN lifetimes against uptake in marine fogs. However, the difference in thermal decomposition rates will be a bigger effect because of the shorter timescales over which thermal decomposition happens.

Table 1. The numbers from Burkholder et al are based on the Kames and Schurath work, so are not independent. Moreover, the uncertainty given by Burkholder et al seems inappropriately high. This may be due to the custom in chemical kinetics evaluations of assigning extra uncertainty when there is only one measurement reported in the literature.

References


Orlando, J. J., Tyndall, G. S., Bertman, S. B., Chen, W., and Burkholder, J. B.: Rate coefficient for the reaction of OH with $\text{CH}_2=\text{C(CH}_3\text{)}\text{C(O)OONO}_2$ (MPAN), Atmos. Environ., 36, 1895-1900, 2002.