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Atmospheric
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Discussions

Interactive comment on "Kinetic double-layer model of aerosol surface chemistry and gas-particle interactions (K2-SURF): degradation of polycyclic aromatic hydrocarbons exposed to O_3, NO_2, H_2O, OH and NO_3" *by* M. Shiraiwa et al.

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General Comments:

The paper by Shiraiwa and co-workers provides a timely compilation of recent experimental heterogeneous PAH degradation studies. The results presented in this manuscript provide a good blueprint for outlining the direction future laboratory studies of PAH degradation (i.e., further reactions with radical oxidants and further competition reactions) should take.

Comment 1:

In Section 3.1.1 (pg 18033 lines 17-21) and Section 3.1.2 (pg 18034 lines18-21), the authors discuss the differences in the kinetics of PAH degradation by ozone observed on solid and liquid substrates. Much of the work presented in Kwamena et al (2006, 2007) focussed on exploring the effect of the substrate on PAH degradation. And in fact, we found the difference in the results of the studies listed at the top and bottom portions of Table 1 of this manuscript to be a result of how the experiment was performed (i.e., whether the experiment was performed on a thin film/air-water interface or on aerosol) and not necessarily because the substrate was a solid or a liquid. To illustrate, in Kwamena et al (2007), the degradation of anthracene by ozone was performed on both phenylsiloxane oil "aerosol" and on a phenylsiloxane oil "thin film." In both cases, the substrate was a liquid yet, the k1max was an order of magnitude higher on aerosol compared to the thin films (refer to Table 4, Kwamena et al (2007)). The exact reason for the difference in the results obtained by the two experimental approaches was not entirely clear. However, in that study, one of the suggestions made to account for the difference was that a greater portion of the PAH concentration was found in the bulk in the thin film experiments compared to the aerosol experiments, given the differences in the surface area-to-volume ratios of the two methods. Since the comparison between solid and liquid aerosol occurs throughout the manuscript, I believe that it is important to point out that the difference in the experimental approaches may be another explanation for the observed differences in the results listed at the top and bottom of Table 1, and as such, perhaps, the aerosol and thin film experiments may be viewed more as upper and lower limits, respectively, for the kinetics of PAH degradation.

Lastly, in the bottom portion of Table 1, the entry for anthracene on phenylsiloxane oil that is quoted is actually the value that was obtained on aerosol. And although this result is viewed as a liquid substrate, the kinetics have perfect agreement with the modelled uptake coefficients for solid soot surfaces in Figure 4. (The red circles representing the results on phenylsiloxane oil aerosol line directly on the red line modelling the uptake coefficient on soot surfaces). This observation is also consistent with my point above that the results on the different substrates may not simply differ by the fact that they are either liquid or solid. It is suggested that in order to compare similar type experiments (i.e, aerosol vs thin film), the entry should be replaced with results from the thin film experiment (see Table 4, Kwamena et al (2007)) or the entry currently in the manuscript should be moved to the upper portion of the table.

Comment 2:

In section 4.2 and Section 4.2.1, the authors model the evolution of surface compositions and uptake coefficients over different timescales. For the PAH-O3-H2O-OH system, the authors suggest that the reaction of PAHs with OH on soot does not affect PAH degradation but that it does significantly affect PAH degradation on organic surfaces. Can the authors speculate as to why soot appears to be a special case compared to the other organic substrates with respect to whether or not O3 or OH is the most important reaction oxidant?

Comment 3:

As mentioned previously, the results of this paper provide a good blueprint for the direction of future laboratory studies and as such a few lines presenting some suggestions for future work in this area would be a good way to end the manuscript.

Technical comment: Page 18032, line 12 – acid is spelled incorrectly.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 18021, 2009.