

Interactive comment on “Kinetic double-layer model of aerosol surface chemistry and gas-particle interactions (K2-SURF): degradation of polycyclic aromatic hydrocarbons exposed to O₃, NO₂, H₂O, OH and NO₃” by M. Shiraiwa et al.

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Response to N. Kwamena

We thank Dr. Nana Kwamena for valuable comments. The constructive suggestions for improvement are very welcome and will be implemented upon revision. Detailed responses to the individual comments are given below.

General Comments:

The paper by Shiraiwa and co-workers provides a timely compilation of recent ex-
C7971

perimental 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.

Response:

Thanks for the positive evaluation of our manuscript.

Comment 1:

In Section 3.1.1 (pg 18033 lines 17-21) and Section 3.1.2 (pg 18034 lines 18-21), 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 k_{1max} 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 modeled 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 modeling 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.

Response:

Thank you for pointing out an interesting issue. We will add a discussion about difference between the particle and thin film experiments in the revised manuscript. We will also point out that the difference in the experimental approaches may be another explanation for the observed differences in the results in Table 1. We will specify in Table 1 which experiments are conducted using aerosol particles. As most are already discussed in Kwamena et al 2007, we will cite this paper properly. Regarding the diffusion of PAH into bulk in thin film experiments, clearly further investigations are needed and we are planning to use a kinetic multi-layer model (Shiraiwa et al., 2009) which resolves bulk diffusion and reaction to resolve these differences. We think the particle experiments were more atmospherically realistic than the thin film experiments, as some PAHs were observed to be dissolved into bulk in thin film experiments. We intend to leave the phenylsiloxane oil entry in the middle section of Table 1, as we do not classify data based on the experimental method, rather classify based on substrates (soot vs. solid organics vs. liquid).

C7973

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?

Response:

The differences of PAH degradation on soot and on the solid organic surface are mainly caused by the different desorption lifetimes of ozone as derived and discussed in Sect. 3 (~10 s vs. ~0.1 s). We speculate that the longer apparent desorption lifetime on soot may reflect stronger electron donor-acceptor interactions between the graphene layers (aromatic rings) and the adsorbed ozone molecules or oxygen atoms, respectively.

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.

Response:

Thanks for the suggestion. We will include such suggestions at the end of the conclusions section: "We propose that K₂-SURF may be used to design, analyze, and interpret experiments for better understanding of heterogeneous reaction systems. For example, systematic sensitivity studies can help to determine the range of experimental conditions (reactant concentrations, reaction time, etc.) that are likely to provide most information and direct insight into possible reaction mechanisms and the underlying physicochemical parameters (e.g., Langmuir-Hinshelwood-type vs. Eley-Rideal-type

C7974

mechanisms, physisorption vs. chemisorption, adsorption/desorption vs. chemical reaction rate coefficients, etc.)”

Technical comment:

Page 18032, line 12 – acid is spelled incorrectly.

Response:

Typo will be corrected.

References.

Kwamena, N. O. A., M. E. Earp, C. J. Young and J. P. D. Abbatt: Kinetic and product yield study of the heterogeneous gas-surface reaction of anthracene and ozone, *Journal of Physical Chemistry A*, 110, 3638-3646, 2006.

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Shiraiwa, M., Pfrang, C., and Pöschl, U.: Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone, to be submitted, 2009.

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