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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Detailed heterogeneous oxidation of soot surfaces in a particle-resolved aerosol model" *by* J. C. Kaiser et al.

Anonymous Referee #2

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Review of Kaiser, et al

This paper uses a state of the art particle resolved model and a detailed heterogeneous chemistry mechanism previously described in the literature to study the oxidation of PAHs on soot particle surfaces. The topic is of interest to atmospheric chemists, the paper is well written, and the assumptions, results, and conclusions discussed adequately. Thus, I recommend publication in ACP after only minor issues are considered for a revised version.

Comments 1. This modeling effort is very nicely done and reveals interesting details about the oxidation mechanisms of PAHs on soot particles. I think the most novel scientific finding (as opposed to new model application) is the importance of NO3 – although I believe the potential importance of NO3 was already discussed in general

by Reisen and Arey, EST 2005 39(1), 64 – 73. I did not see a reference to this work, or generally, constraints from field observations on the overall applicability of this modeling effort. I think the paper would improve by at least discussing briefly the model results in the context of observations of PAHs. I realize the model is not set up to compare directly with any observations, but instead to analyze in general the lifetimes and likely products. But, there would still be some utility in noting that nitro-PAHs are detected, e.g. with evidence of NO3 radical chemistry (though also via OH chemistry – implying gas-phase PAH oxidation channels for more volatile species as expected) etc.

2. In the abstract, the lifetimes of PAHs on soot particles is reported as derived from the model for ozone, NO2, OH, and NO3. However, it is not very clear that these lifetimes are only for PAHs absorbed at the surface of the soot particle. Without carefully reading the manuscript, one could easily misinterpret these values to assume that PAHs have a very short atmospheric lifetime (which is obviously not true given their transport days downwind of source regions). This issue should also be discussed again in the conclusions section as well. It implies that condensation of other gases (as noted in the text) is important for blocking the oxidation process, or that PAHs exist buried within particles in a manner inaccessible to atmospheric oxidants.

3. It seems there is a general assumption that the oxidation products are less volatile and thus remain on the surface. For understanding oxidation of the initial surface bound PAHs only, this assumption isn't so important, but it would matter in a complete treatment of oxidation of PAHs throughout the particle bulk during the course of a particle's atmospheric lifetime. Volatilization of some products would then potentially allow oxidation of PAH's below the surface more feasible. I may have missed a discussion of such a possibility in the paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 5127, 2011.