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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.

Anonymous Referee #2

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First, let me state that I think it is not just ambitious, but admirable that the authors attempt to create a general prescription for interfacial reactions. I do worry somewhat that the output of such models may be (erroneously) overinterpreted, but I do acknowledge that it is necessary to start somewhere. To my knowledge, this is the first treatment which deals with multiple adsorbants / reagents – another strong point, but also adding to the complexity and thus possible misinterpretations of fitted/predicted results.

That said, I do have a few concerns about this manuscript, detailed below.

1) McCabe and Abbatt (J. Phys. Chem. C 2009, 113, 2120–2127) in their Fig. 6 present a similar figure to Fig. 4 here, as well as some speculations concerning what governs heterogeneous ozone-organic reactivity. I think this should be somehow discussed here.

2) Kwamena et al. (2007) discusses the substrate dependence of O3 + anthracene at some length. Again, I believe this discussion is germane to proper interpretation of the model presented here (and its derived parameters).

3) Mmereki et al. (2004) present results for anthracene reactions on water surfaces – both pure and those coated with a monolayer of organic – NOT pure organics, as implied here. The differences in rates among the different coatings reflect differences in both ozone surface partitioning and reactivity ... .implying some chemical specificity which is not captured by the model. This kind of thing is why I worry about overinterpretation.

4) The ozone desorption lifetimes for liquid surfaces presented here may be compared to those computed by MD calculations – the latter are much faster (see Vieceli et al, J. Phys Chem. B 2005, 109 15876-15892) but do capture the difference between pure water and water with an organic coating. My feeling is that we are all missing some fundamental aspect of the physical chemistry of these reactions, but so far, no-one has really identified where we are going astray.

5) All the ozone partitioning seems to be based on the area per adsorbed molecule inferred experimentally from soot adsorption. The PAH (and other organic) adsorption "areas" seem to be based on a "shoulder-to-shoulder" coverage ideal for these compounds – independent of the substrate. This implies that condensation of the organic is wat governs its partitioning to the surface – and not any specific interactions with the substrate. This concept seems somewhat at odds with what (little) we actually know (c.f. Kwamena et al, 2007)

I also have some more minor quibbles, but I do think that this framework concept is important to be widely accessible, to encourage thought and debate about how to think about surface processes, so these are not so critical.

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