

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.

M. Shiraiwa et al.

m.shiraiwa@mpic.de

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Response to Referee #2

We thank anonymous Referee #2 for the review of our manuscript. The constructive suggestions for improvement are very welcome and will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee Comment 1:

First, let me state that I think it is not just ambitious, but admirable that the authors at-C7981

tempt 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.

Response:

Thanks for the constructive feedback. The concerns will be addressed below and in the revised manuscript.

Referee Comment 2:

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.

Response:

Many thanks for pointing this out. We will add the following paragraph in Sect. 3.1.2 of the revised manuscript. “McCabe and Abbatt (2009) have already pointed out a remarkable similarity of γ_{O_3} on a variety of surfaces (soot, 1-hexadecene, metal oxides, atmospheric mineral dust, PAHs coated to soot, organic, and water substrates) both in their absolute magnitude and in their partial pressure dependence, especially given the very different experimental techniques (Knudsen cells, aerosol flow tubes, etc.). Possible explanations and rate limiting steps discussed in their and earlier studies are: surface diffusion of adsorbed ozone molecules (Kwamena et al., 2007) and/or multiple steps of chemical reaction involving possible intermediates like O₃⁻ ions (Nelander and Nord, 1979) or O atoms (Stephens et al., 1986; Pöschl et al., 2001; Sullivan et al., 2004). “

Referee Comment 3:

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).

Response:

Following your suggestion and the comment by N. Kwamena, we will add the discussion of substrate effect in Sect. 3.1.1 in the revised manuscript. "Kwamena et al. (2007) pointed out that the substrate influences the partitioning of ozone to the surface irrespective of the PAH adsorbed to it. They also suggested that different experimental approaches can yield different results. In particular, they found that PAHs may dissolve into the substrate of thin film experiments, thereby affecting the reaction kinetics and partitioning of O₃ as will be discussed below. "

Referee Comment 4:

Mmerekı 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.

Response:

We will clarify that substrate used in Mmerekı et al (2004) is not pure organics but monolayer on water in text and Table 1. We agree that the differences in rates among the different coatings reflect differences in both ozone surface partitioning and reactivity. We also suspect that some PAH was dissolved in water and bulk reaction between PAH and O₃ occurred. This effect is beyond this K2-SURF study but we intend to investigate this effect using kinetic multi-layer model (Shiraiwa et al. 2009) which couples surface and bulk chemistry. We will also add the following statement in the abstract

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and conclusions: Note, however, that the exact reaction mechanisms, rate limiting steps and possible intermediates still remain to be resolved (e.g., surface diffusion and formation of O atoms or O₃⁻ ions at the surface).

Referee Comment 5:

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.

Response:

Thanks pointing this out. We intend to add the following text in the revised manuscript: According to molecular dynamics (MD) simulations the desorption lifetime of ozone on at the interface of pure water and air should be only 36 ps (Vieceli et al., 2005) which is much shorter than the values listed in Table 1. Possible explanations for the differences are: 1) The surfaces considered in our study are covered by PAH molecules and thus likely to interact differently with ozone. 2) The desorption lifetimes calculated from measurement-derived adsorption constants depend inversely on the assumed surface accommodation coefficients ($\alpha_{s,0}$) and might thus be up to three orders of magnitude shorter if $\alpha_{s,0}$ were close to unity. 3) The chemical species actually residing at the surface might be O atoms rather than ozone molecules, and thus additional processes such as a dissociation reaction or other intermediate steps of chemical interactions at the surface might have to be considered for full mechanistic understanding. 4) Surface-bulk exchange as well as mass transport and chemical reactions might also play a role for liquid substrates. Further investigations will be needed to resolve these issues, and we are planning to pursue such investigations using K2-SURF as well as kinetic double- and multi-layer models that resolves also diffusion and reaction in the bulk of

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the particle or substrate, respectively (K2-SUB, Pfrang et al., 2009; KM-SUB, Shiraiwa et al., 2009).

Referee Comment 6:

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 what 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.

Response:

We use effective molecular cross sections rather than an idealized ‘shoulder-to-shoulder’ coverage. As pointed out, we do not resolve the specific interactions between organics (PAH) and substrate in this study. In principle, however, the PRA framework and K2-SURF would allow to account for such interactions if suitable information and parameters were available. As specified by Pöschl et al. (2007) (P5995 after Fig. 2 and P5998 after eq(36)):

“To describe surface-bulk mass transport and the potential influence of bulk composition on surface processes, it is useful to define the condensed phase directly adjacent to the quasi-static surface layer as the “near-surface particle bulk”. Depending on the chemical composition and physical state of the investigated particles, the near-surface bulk region can be pictured to extend one or a few molecular diameters or chemical bonds (~ 1 nm) from the quasi-static surface into the particle bulk. The chemical species present in the near-surface particle bulk are not directly exposed to the gas phase or sorption layer species, but they interact with the quasi-static surface layer and

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can influence its physicochemical properties: e.g. electron donor-acceptor and charge-transfer interactions; hydrogen bonding networks (O’Hanlon and Forster, 2000); quasi-liquid or structurally disordered surface layers on ice (Delzeit et al., 1996; Girardet and Toubin, 2001).”

“If the surface accommodation process were significantly influenced not only by the quasi-static surface layer but also by the underlying condensed phase (e.g. by hydrogen bonding or other electron donor-acceptor interactions), the composition of the near-surface particle would also have to be taken into account. This could be achieved by expressing $s_{i,0}, X_i, Y_p$ as a linear combination of the adsorption probabilities $s_{i,0}, X_i, Y_p, Y_q$ which would be observed for X_i colliding with an adsorbate-free surface made up of pure Y_p on an underlying bulk of pure Y_q : eq (37). The weighting factor Y_q could be the mole, mass, or volume fraction of Y_q in the near-surface particle bulk. The latter appear to be more suitable for the representation of macromolecular particle components.”

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