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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 #1

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Referee general comment:

Heterogeneous oxidation is an important process in atmospheric chemistry because it can influence toxicity and cloud condensation nuclei ability of aerosol particles. The authors simulate the chemical transformation of PAH on soot by O3, NO2, OH and NO3 using the particle-resolved aerosol model PartMC-MOSAIC. The authors present a chemical lifetime of PAH on soot in different relative humidity and NOx emission levels, which can be used as parameterizations in large-scale climate models. The results are highly interesting and the paper represents a substantial contribution to scientific progress within the scope of ACP. The paper is presented in a clear and well-structured way. Some of the scientific messages, however, are similar/equivalent to those of related earlier studies. As detailed below, the authors may specify more clearly, in

which way their findings and messages confirm and extend those of earlier studies. I recommend it for publication in ACP after the following suggestions for improvement have been addressed.

Specific comments:

- The authors report a range of 2×10-7 - 2×10-6 for the uptake coefficient of ozone (γO3) on PAH-coated aerosol particles. As shown in Fig. 3, γO3 is initially as high as 10-5 and drops to 10-6 after degradation of the PAHs. Thus, 2×10-7 - 2×10-6 seems characteristic for the uptake of ozone by oxidized PAHs (Y2,Y3). The authors may address and clarify these aspects.

- In section 4.3, the authors compared their results with Springmann et al. (2009) and Pöschl et al. (2001). Please also compare with Shiraiwa et al. (2009), who demonstrated the PAH half-life on soot can be below ten minutes during nighttime (Fig. 9) due to NO3. They also suggested that OH has a minor contribution and O3 plays a dominant role in PAH degradation on soot.

- Recently, Shiraiwa et al. (2011) showed the formation of long-lived reactive oxygen intermediates upon heterogeneous reaction between ozone and PAH. The desorption lifetime of ozone is actually much shorter (nanoseconds, but not seconds) and ozone decomposes into O atom, which are long-lived and reactive towards PAH. The apparent long desorption lifetime of ozone (10 s) includes the adsorption and decomposition of ozone. This possibility had been mentioned in earlier studies (e.g., Stephens et al., 1986, Rogaski et al.,1997, Pöschl et al., 2001), and it may be worthwhile to mention this aspect and that the kinetics of heterogeneous reactions can be described at different levels of mechanistic detail.

References:

Pöschl, U., Letzel, T., Schauer, C. and Niessner, R.: Interaction of ozone and water vapor with spark discharge soot aerosol particles coated with benzo[a]pyrene: O3 and

H2O adsorption, benzo[a]pyrene degradation, and atmospheric implications, J. Phys. Chem. A, 105, 4029-4041, 2001.

Rogaski, C. A., Golden, D. M. and Williams, L. R.: Reactive uptake and hydration experiments on amorphous carbon treated with NO2, SO2, O3, HNO3, and H2SO4, Geophys. Res. Lett., 24, 381-384, 1997.

Shiraiwa, M., Sosedova, Y., Rouviere, A., Yang, H., Zhang, Y., Abbatt, J. P. D., Ammann, M. and Pöschl, U.: The role of long-lived reactive oxygen intermediates in the reaction of ozone with aerosol particles, Nature Chem., 3(4), 291-295, 2011.

Shiraiwa, M., Garland, R. M. and Pöschl, U.: 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, Atmos. Chem. Phys., 9, 9571-9586, 2009.

Stephens, S., Rossi, M. J. and Golden, D. M.: The heterogeneous reaction of ozone on carbonaceous surfaces, International Journal of Chemical Kinetics, 18, 1133-1149, 1986.

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