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Atmospheric
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Discussions

Interactive comment on "Artifacts in measuring aerosol uptake kinetics: the roles of time, concentration and adsorption" *by* L. H. Renbaum and G. D. Smith

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Referee general comment:

This paper addresses an important issue of organic aerosol chemistry. The oxidation experiments of organic aerosol are usually conducted employing high concentration of oxidants and short reaction time. The experimental results are often extrapolated to atmospheric conditions, assuming that time and concentration are interchangeable variables, even though this has not been established well. Here the authors studied the kinetics of radical oxidation reaction of organic aerosols by varying separately the radical concentration and the reaction time. They conclude that indeed concentration

and time are interchangeable parameters. The experiments were executed very well, the results are interesting and presented clearly. However, I have some concerns which the authors should consider as specified below. I recommend it for publication in ACP after the following comments for improvement/suggestions have been addressed.

Specific comments:

1. Do authors have any information on particle or oxidant loss to the wall? The effects of wall might be larger in the large flow tube reactor compared to the small one because the residence time of particles is long. Do authors think this may potentially affect the observed reaction kinetics or this wall effects are negligible?

2. I am concerned that the authors did not correct for gas-phase diffusion of the radical to the particle. The gas phase diffusion correction is indeed negligible if uptake coefficients is below 10ˆ-3, but it is significant with uptake coefficients over 0.1 for the particles larger than 100 nm (Pöschl et al., 2007 and see Fig. 2 in Shiraiwa et al., 2009). The authors should either apply a gas phase diffusion correction, or otherwise justify why this correction is not needed.

3. The authors applied Langmuir-type isotherm to the experimental data. Do the authors implicitly assume that kinetics is limited by surface adsorption/reaction and ozone dose not diffuse into the bulk?

4. The high K value of 10ˆ-15 cm3 suggests the high surface coverage and long desorption lifetime (about millisecond to second) of O3 (Kwamena et al., 2007; Shiraiwa et al., 2009). The molecular dynamic simulation predicts that desorption lifetime of O3 on liquid particle should be only about nanoseconds (Vieceli et al. 2005). Recently, Shiraiwa et al. (2011) showed the formation of long-lived reactive oxygen intermediates (ROIs) upon heterogeneous reaction of ozone. The desorption lifetime of ozone is actually short (nanoseconds, but not seconds) and ozone decomposes into ROIs (O atom), which are long-lived leading to the high surface coverage. It may be worthwhile to discuss this aspect.

5. The authors conclude that time and concentration are interchangeable variables. I am concerned how robust this conclusion is. The reaction time of 66 s is still too short compared to atmospheric oxidation time of hours to days. Therefore, the reactants were consumed only 20%. Are the authors sure that the conclusions hold if the reactants are consumed for example 90% or more? Please note that uptake coefficients are not constant but function of reaction time and concentration of reactants (Ammann and Pöschl, 2007). I do agree with the authors that more work is needed to explore the effects of chemical and physical properties of particles such as phase state (e.g., liquid vs. semi-solid vs. solid).

References:

Ammann, M. and Pöschl, U.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 2: Exemplary practical applications and numerical simulations, Atmos. Chem. Phys., 7, 6025-6045, 2007.

Kwamena, N. O. A., Staikova, M. G., Donaldson, D. J., George, I. J. and Abbatt, J. P. D.: Role of the aerosol substrate in the heterogeneous ozonation reactions of surface-bound PAHs, J. Phys. Chem. A, 111, 11050-11058, 10.1021/jp075300i, 2007.

Pöschl, U., Rudich, Y. and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989-6023, 2007.

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.

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.

Vieceli, J., Roeselova, M., Potter, N., Dang, L. X., Garrett, B. C. and Tobias, D. J.: Molecular dynamics simulations of atmospheric oxidants at the air-water interface: Solvation and accommodation of OH and O3, J. Phys. Chem. B, 109, 15876-15892, 2005.

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