Atmos. Chem. Phys. Discuss., 11, C4127–C4128, 2011
www.atmos-chem-phys-discuss.net/11/C4127/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical ageing and transformation of diffusivity in semi-solid multi-component organic aerosol particles" *by* C. Pfrang et al.

Anonymous Referee #1

Received and published: 31 May 2011

This manuscript presents a logical development of recent work by the authors in simulating the time dependence of heterogeneous chemistry in well-defined systems of atmospheric relevance studied through controlled laboratory measurements of aging. The unique focus of this manuscript is the influence of decreasing diffusivities of reactants within a particle on the lifetime and timescale for chemical transformations to occur. In particular, the reaction of oleic acid with ozone is considered, where the particle consists of a mixture of components and for which a decrease in diffusivity over time is explored following the formation of oligomers. In some ways, the manuscript feels fairly incremental, considering a coupling of the diffusivity to composition while neglecting key processes such as the volatilization of products and the partitioning of

water to the particle as the chemical makeup changes. The impact of the manuscript would be much more significant if the heterogeneous aging were coupled to these two processes.

The authors should address the following comments before the manuscript is accepted for final publication.

(1) The authors consider the implications of this work for atmospheric aerosol. My concern is that this section is compromised to a great extent by the neglect of volatilization and hygroscopicity. The loss of volatile products and the absorption of water would both lead to changes in particle composition and changes in diffusivity. The authors should discuss the limits of their model more clearly, defining the conditions under which the model predictions may be considered to be accurate and relevant to the atmosphere, and highlighting the potential impact of considering the loss of volatiles and hygroscopic growth on the chemical ageing.

(2) On page 13011, final line, the authors refer to a parameter that defines the degree of solidification. This parameter must be defined clearly in the main body of the manuscript and limiting values discussed, particularly describing how this is related to the change in diffusivity and the formation of a 'crust'.

(3) I am concerned that the authors may be over interpreting experimental data. In Figures 1(a) and (b), the interpretation of the experimental data appears to rely on the accuracy of two data points alone, the longest time points in both figures. How reliable are these measurements? What level of accuracy can really be achieved in inferring the decreasing diffusivity from these measurements, a few orders of magnitude? This is particularly important given that the model does not consider the evolving composition through loss of volatiles that is undoubtedly happening in the actual measurement.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 13003, 2011.