

## ***Interactive comment on “Validation of an experimental setup to study atmospheric heterogeneous ozonolysis of semi-volatile organic compounds” by M. Pflieger et al.***

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The paper by Pflieger and coworkers adds to the growing number of studies investigating the heterogeneous reactions of SVOCs, PAHs in particular, and describes the development of a new experimental technique to investigate these heterogeneous reactions. Some of the conclusions drawn by the authors regarding the mechanism governing the kinetics of the reaction seem to be inconsistent with the data that is presented. In addition, although there is indeed a need for improvement as to how heterogeneous reactions of SVOCs are probed, the technique presented in this paper still suffers from the disadvantages that plague offline analysis techniques and as such

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the improvements gained by this technique have not been adequately highlighted.

On the use of the Langmuir-Hinshelwood: The kinetics appear to be done based on two time points; time zero and a later time point. Were there any experiments performed where multiple time points were obtained for a given ozone concentration to confirm that the kinetics were indeed following pseudo-first order behaviour? Further, based on the data in Figures 4a and 4b it seems inappropriate to attempt to fit the data to the Langmuir Hinshelwood (L-H) equation, especially for the data presented in Figure 4a. How do the regression coefficients of the L-H fits compare to those of the linear regression? For the experiments performed on XAD-4, it appears that more experiments should be performed before any conclusions can be drawn about the nature of the dependence of  $k_{1exp}$  as a function of ozone concentration.

Further, it is suggested that the reaction on silica and XAD may follow the L-H mechanism at higher concentrations but experiments were not performed at higher ozone concentrations because they were not atmospherically representative. However, in order to get a clear picture of the mechanism it is necessary to extend the ozone concentrations over which the experiments were performed to ensure that the  $k_{1exp}$  values would indeed reach saturation instead of speculating on the behaviour at these higher concentrations.

The discussion on the influence of the substrate presented on page 19186 lines 20 to 27 does not seem to be appropriate given that the data in Figures 4a and 4b does not convincingly support the L-H mechanism. Based on the data and analysis presented in the paper, a more appropriate discussion would be to expand on the differences in the second order rate constants obtained for the reaction of naphthalene on silica and XAD-4 particles using the Eley Rideal mechanism. Therefore, the discussion on page 19185 line 26 to page 19186 line 7 should be expanded upon.

On the experimental technique: The authors have developed a new technique to investigate the heterogeneous reactions of SVOCs. Much of the previous work in this

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area used offline analysis methods which suffer from positive and negative artefacts. The technique presented in this manuscript offers a new variation but still requires solvent for particle deposition, which may modify the particles' properties, and relies on offline analysis techniques to determine the un-reacted naphthalene after exposure to ozone. The overall technique is quite similar to those used in other kinetic studies in the literature. The authors have not clearly articulated the improvements offered by their technique.

The silica and XAD-4 particles used in this paper are coated by vapour deposition, which as the authors suggest is more representative of how PAHs may be deposited onto particles in the atmosphere. However, there have been a number of studies that have used vapour deposition to coat aerosols to which the authors fail to include in their review of previous work (page 19175 line 26 to page 19176 line 4) investigating heterogeneous reactions of SVOCs, PAHs in particular. Some of the omitted work includes studies looking at the heterogeneous reactions of PAHs and ozone by Pöschl et al. on soot aerosols [1]; by Kwamena et al. on dicarboxylic acids [2, 3], sodium chloride [2] and phenylsiloxane oil [3] aerosols; by Gloaguen et al. on sodium chloride [4] or by Mmereki et al. at the air-water interface [5, 6]. In addition, some of these previous works have been done online and in real-time [4-8] thus avoiding the problems associated with offline analysis. The authors should put their technique in the context of these previous works and describe in greater detail, the advantages of their own method.

A reference omission: The authors mention the paper by Pöschl et al. [1] on page 19183 line 14 but the full reference is not listed in the References section.

#### REFERENCES:

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