

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

**M. Pflieger et al.**

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### **REPLY TO ANONYMOUS REFEREE 1**

**Answer to Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19173, 2008.**

The aim of this work was to develop an *alternative* device to provide results on heterogeneous kinetics of semi-volatile organic compounds (e.g. pesticides) that presumably exhibit extremely slow reactivity towards the atmospheric oxidants such as ozone and OH. Therefore, the aim was not the development of a highly sophisticated experimental device but rather to focus on an experimental procedure which is adapted to study slow reactivity. Naphthalene was chosen as a test compound because it was widely studied in the past and thus it represents a good reference. The text has been accordingly

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modified. The amount of adsorbed naphthalene is well below the number of adsorption sites on the solid support (silica or XAD-4). This observation can arguably be interpreted as multilayer naphthalene coverage on the few first millimeters of the length of the reactor. However, we have verified that during the deposition process a large part of gaseous naphthalene passed through the reactor. Since we detected gaseous naphthalene at the outlet of the reactor we cannot assure a uniform distribution of naphthalene on the aerosol surface but we can reasonably assume that adsorption occurred all along the reactor tube. Taking this assumption in account, our calculations based on the spherical geometry of the molecules, indicates that we are well below a monolayer coverage (0.6% and 0.002% for silica and XAD-4 particles, respectively). This information has been added in the paper. In the previous version of the manuscript, we only fitted  $K_{O_3}$  while  $k_{max}^I$  remained fixed at the  $k_{obs}^I$  value obtained at the highest studied ozone concentration. The Langmuir-Hinshelwood curve has been improved by fitting two parameters:  $K_{O_3}$  and  $k_{max}^I$  giving better coefficient regression ( $R^2=0.99$  and  $0.83$  for silica and XAD-4 particles, respectively). These changes have been included in the manuscript. In addition, we agree that our experimental data do not allow one to distinguish between the Langmuir-Rideal and the Langmuir-Hinshelwood mechanism. To do so, it would be necessary to inject ozone concentrations of at least an order of magnitude higher than what was done. However, our device does not allow working at ozone concentrations higher than 40 ppm. Moreover, giving a clear picture of the mechanism was not the scope of the paper. The experimental procedure was developed to study the heterogeneous kinetics of slowly reactive semi-volatile organic compounds in order to estimate their atmospheric lifetimes. Accordingly, it is not necessary to distinguish the mechanisms since there is not a significant difference between the two naphthalene's lifetimes calculated using both mechanisms under atmospherically relevant ozone concentrations. The discussion section has been accordingly modified.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19173, 2008.

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