

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

Anonymous Referee #1

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This paper presents a new approach to measure the reactivity of adsorbed (organic) molecules on particulate surfaces that are mounted on a flow tube wall. In particular, the particulates are exposed to a steady flow of gas-phase organics which leads to the organics being adsorbed. Then, a gas-phase oxidant, in this case ozone, is exposed to the coated particulates. Standard chromatographic methods are used to analyze the amount of organic remaining, and so heterogeneous decay kinetics can be monitored. In this regard, the analytical chemistry aspects of the paper are fine.

Experimentally, my major concern is that the organics are not homogeneously distributed on the particulates lining the flow tube walls. While the authors claim the

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coverage is sub-monolayer, is there any evidence that it is uniform, both with respect to the depth of the mounted particulates as well as axially down the length of the flow tube?

I have major problems with the data analysis. Looking at the data in Figure 4, there is no way that a Langmuir-Hinshelwood mechanism is justified; there is no indication of saturation in the kinetics and the ozone range explored is not high. Indeed, to justify an Eley-Rideal mechanism, it would be necessary to take the ozone pressures to higher values to see if there is a saturation in the kinetics or not. The entire data analysis section needs to be re-written to point out that no statement about mechanism can be stated with confidence.

Overall, this is a fair paper. The experimental technique is not as sophisticated as those currently being used in the field in the past few years, which use aerosol particles. And the data analysis is naive. From a results perspective, it is hard to know if the kinetics are slow because the surfaces coverages are indeed submonolayer or not. Earlier work in this field, using similar approaches, has shown that if supermonolayer coverages are used, then slow kinetics are observed.

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

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