

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 #2

Received and published: 9 December 2008

This paper introduces a new experimental approach to determine the heterogeneous ozonolysis of naphthalene. This study involves a novel flow reactor system which provides a high trapping efficiency for PAHs. The loss of naphthalene by reaction with ozone is monitored. The reactive uptake kinetics are interpreted with respect to a Langmuir-Rideal and Langmuir-Hinshelwood mechanism. The paper addresses relevant scientific questions within the scope of ACP.

This paper is not publishable in its current form. The reasons for this decision are outlined below in more detail. A re-analysis of the experimental data might be necessary which subsequently would affect the results and conclusion of this manuscript. The

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manuscript will benefit by clarification of this issue, however, additional major revisions are necessary for publication.

General comments:

1. My major criticism concerns the analysis of the experimental data. The presented experimental approach appears to be similar to coated-wall flow tube reactor experiment. The inside wall of the exterior tube is specifically treated by a coating of particles to achieve a higher trapping efficiency of naphthalene. The inner volume of the flow reactor is blocked by an interior concentric glass tube. The manuscript contains many typographic errors; this includes the statement about the distance between these two tubes. The dimensions of the concentric tubes suggest a distance of 0.5 cm and not as stated of 0.5 mm. Naphthalene will adsorb on both of these walls. No information is given on the pressure within the flow reactor. Such flow reactor experiments are usually conducted under low pressure conditions to minimize diffusion of the gas phase reactants since the reactive surface is a few millimeters away from the center of the gas flow. Assuming a pressure of about 1 atm and a distance of about 0.5 cm, the reaction kinetics may be diffusion limited. If the distance between the two reactive walls is only 0.5 mm, the effect may be smaller, but still significant. (How is the flow reactor assembled without damaging the particle coating if the width is only 0.5 mm?) The presented experiment is possibly more complicated than a common coated-wall flow reactor since two different walls with different surface areas are applied. In addition, since the naphthalene covers less than 1% of the available surface area, ozone may also react with the silica particles, i.e. for one of the surfaces there is a competitive reaction occurring. This complicates the overall uptake process: a) there might be local areas with different ozone concentrations. b) what is the actual amount of ozone reacting with naphthalene? c) possibility that the observed k value does not represent the truth reaction rate since the reaction might be diffusion limited. For these reasons the derived k values may not be applied to interpret the data.

These issues have to be addressed before possible publication.

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2. More reactive uptake experiments are needed to falsify if the experiments applying XAD-4 particle as a substrate are following a Langmuir-Rideal or Langmuir Hinshelwood mechanism.

3. In the introduction I miss the references to the studies of Poschl et al. 2001, and e.g. the reviews by Rudich 2003, Donaldson and Vaida, 2006, Rudich et al. 2007. These and others should be used to motivate this work.

4. It is strongly recommended that a native English speaker revises the manuscript.

Specific comments:

Page 19180, line 8: Surface area. What is the error in surface area when assuming that the particles are densely packed on the glass walls, possibly lying in grooves from the etching, and stacked in multilayers? Most likely only a small fraction of each particle surface is available for naphthalene adsorption.

How is the XAD-4 surface area determined and how can the overall surface area of XAD-4 particles be larger than the one for silica particles? The XAD-4 particles are orders of magnitude larger than the silica particles (as give in the text) and thus its surface-to-volume ratio is smaller. Also, $0.25 \text{ g} \times 260 \text{ m}^2 \text{ g}^{-1}$ is 65 m^2 and not 64 cm^2 . What is the surface area of the inner glass tube available for naphthalene adsorption? This will affect the overall naphthalene surface coverage as well.

Page 19180, line 26: Change dioxygen to oxygen.

Page 19181, line 4: Elaborate on instantaneous ratio concentrations ozone/PAH. Do you mean the time to reach stable flow conditions and thus stable ozone concentrations? Once the flow is adjusted ozone concentrations should be constant.

Page 19182, line 4: What is the limit of quantification? Do you mean the detection limit? Is it 6.4×10^4 micro gr or 6.4×10^{-4} micro gr?

Page 19185, chapter 4.1:

It is not clear if the ozone concentrations fluctuate within seconds or within minutes during the exposure experiments. Maybe a plot of ozone concentration versus time would be helpful for the reader to understand the ozone averaging procedure.

The data by Michel et al. and Usher et al. show that ozone reacts with the uncoated silica particles. This would imply that the ozone concentration measured in the experiments is not the ozone concentration which reacted with naphthalene. This is in particular true if ozone with silica surfaces reacts faster than ozone with naphthalene. Since less than 1% of the available surfaces are coated by naphthalene, silica surfaces can provide a significant loss of ozone compared to reaction with naphthalene. This affects your derivation of k . I do not see how this additional reaction can explain significant reaction of naphthalene without ozone as shown in Fig. 4. Please elaborate on this. The change in ozone concentration has to be accounted for in the data analysis.

Page 19186, chapter 4.2:

It can not be stated that the experimental data points for the case of the XAD-4 particles are better represented by a Langmuir-Hinshelwood mechanism instead by a Langmuir-Rideal process. Even if the authors would have presented a thorough statistical analysis to prove the superiority of one model versus the other, I suggest to conduct more reactive uptake experiments before any conclusion can be drawn. Why did the authors perform only 4 experiments using XAD-4 versus 8 using silica?

Page 19189, line 5-11: There are several issues with this paragraph: The two different cases, silica versus XAD-4, are not discriminated. The reaction proceeds either via a Langmuir-Rideal or a Langmuir-Hinshelwood mechanism. The data in Fig. 4 does not support any of these statements.

Technical comments:

Some references state the issue number but not the volume number of the journal.

Tables:

Table 1: Please state the concentration of naphthalene determined in both flow reactor as well (inclusive error etc.).

Figure 1: Where is outlet and inlet of the gas flow? Dimensions?

Figure 4: Indicate in both figures the regressions lines.

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

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8, S9736–S9740, 2008

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