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Comment

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.

Received and published: 3 February 2009

REPLY TO ANONYMOUS REFEREE 2

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

ANSWER:

General comments:

1. A) The inside wall of the exterior tube is specifically treated by a coating of particles to achieve a higher trapping efficiency of naphthalene: The interior wall of the exterior tube is not specifically treated by coated particles to achieve a higher trapping efficiency of naphthalene. Our experimental approach was aimed at studying

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the heterogeneous reactivity of naphthalene, which was adsorbed via a gas-solid equilibrium on particles surface. If naphthalene was directly adsorbed on the reactor's wall, we could not investigate the influence of the particles on the naphthalene's reactivity. Moreover, the heterogeneous reactions of ozone with naphthalene directly coated on the glass-wall of the reactor would not correspond to atmospherically relevant conditions.

B) The manuscript contains many typographic errors; this includes the statement about the distance between these two tubes: We agree that there is a mistake in the manuscript concerning the distance between the two reactor's tubes. The right distance is actually 0.5 cm and this typing error has been corrected in the text. Therefore, the flow reactor is easily assembled without damage.

C) Naphthalene will adsorb on both of these walls: Only the internal wall of the external tube is of concern here. The presence of the internal tube permits to minimize the interannular space to make sure the kinetics are not diffusion limited (see below). Particles are only applied on internal wall of the external tube. It is true that some naphthalene can be adsorbed on the internal tube, but it was not extracted because the internal tube was removed prior to the extraction procedure. We have added this information in the text.

D) No information is given on the pressure within the flow reactor: We worked at atmospheric pressure.

E) Such flow reactor experiments are usually conducted under low pressure conditions to minimize diffusion of the gas phase reactants since, etc.: We would like to emphasize that we did not investigate reactive uptake experiments. We followed the consumption of naphthalene during different exposure times and under different ozone concentrations. Our experiments last much longer than reactive uptake studies. The diffusion phenomenon ought to be taken into account but it is not a limiting factor under our experimental conditions. The diffusion coefficient of ozone in nitrogen is 0.148

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$\text{cm}^2 \cdot \text{s}^{-1}$ (at 1 atm and 298 K) (Fuller et al., 1966). In our reactor (interannular space = 0.5 cm), the diffusion time is 3.4 s which is lower than the residence time (7.5 s) of the gas in the reactor and much lower than the exposure times (12–204 min). As a result, the reaction is not diffusion limited. This additional information has been included in the text.

F) In addition, since the naphthalene covers less than 1% of the available surface area, ozone may also react with the silica particles, etc.: Ozone can react with silica surfaces, and therefore we carefully checked this possibility. After the performed measurements we could not see a significant difference between inlet and outlet ozone concentrations. These measurements were performed with high ozone concentrations (about 10 ppm). Although a small amount of ozone is taken up by silica surface, this phenomenon does not change the mean ozone concentration to which naphthalene was exposed.

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: One of the goals was to observe if the nature of the particles shows an influence on the kinetics. However, we only performed four experiments on XAD-4 particles because this support is not atmospherically relevant. Moreover, we agree that our experimental data do not allow one to distinguish between the Langmuir-Rideal and the Langmuir-Hinshelwood mechanisms. However, to give a clear picture of the mechanism was not the scope of this paper. The experimental procedure was developed to study the heterogeneous kinetics of slowly reactive 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.

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.

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2007: The missed references have been added in the introduction (Pöschl et al, 2001; Rudich, 2003; Rudich et al., 2007, Donaldson and Vaida, 2006).

4. It is strongly recommended that a native English speaker revises the manuscript: The English language usage was carefully checked.

Specific comments

Page 19180, line 8: It is not possible to determine the exact surface area available for naphthalene adsorption because particles possibly form aggregates. Even if we estimate that only 1/10 of the total particles surface is available, we remain below a monolayer coverage. The recovery would be 0.02 and 6% for XAD-4 and silica particles, respectively. The specific surface of XAD-4 is $72500 \text{ m}^2 \cdot \text{g}^{-1}$ because of the crushing operation. This information has been added in the text. The surface area of silica particles has been corrected: it is actually 65 m^2 . The surface area of inner glass tube does not affect the naphthalene surface coverage because we do not consider this inner tube (see above answer C) to the general comments 1).

Page 19180, line 26: Dioxygen has been changed to oxygen

Page 19181, line 4: We simply verified that ozone was in excess. We changed the sentence in the text.

Page 19182, line 4: First, $6.4 \times 10^4 \mu\text{g}$ has been changed to $6.4 \times 10^{-4} \mu\text{g}$. Below the quantification limit, the quantification is not possible but only the detection is possible: in this case, a narrow peak appears on the chromatogram, but it cannot be integrated. In our chromatograms, the quantification limit is equal to the detection limit. This detail has been added in the text.

Page 19185, chapter 4.1: Ozone level fluctuates at the beginning and at the end of experiment. An example is given in the following Figure 1. This Figure, entitled 'Ozone concentrations recorded during an experiment of 12 minutes ($[\text{O}_3]_{\text{median}}$: 3,32 ppm and $[\text{O}_3]_{\text{mean}}$: 3,07 ppm)', is available on the following link: <http://www.univ->

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provence.fr/gsite/document.php?pagendx=6832&project=lcp-ira. (Reply to ACPD). It is the reason why we preferred median ozone concentrations instead of mean ozone concentrations. Ozone can react with the uncoated silica particles. To check this possibility we performed blank experiments i.e. the reactor's walls were coated with uncoated silica particles. The latter experiment did not show a significant difference between inlet and outlet ozone concentrations (see above answer F) to the general comments 1).

Page 19186, chapter 4.2: The goal of our experiments was not to show the superiority of one mechanism related to the other but to compare the results of two kinds of experiments (with silica and with XAD-4). For atmospherically relevant ozone concentrations, the two mechanisms provide a similar result, but at higher ozone concentrations the rate constant values corresponding to LH and LR mechanism would differ. We changed the sentence in the text. We only performed 4 experiments because XAD-4 particles are not atmospheric relevant (see answer to the general comments 2).

Page 19189, line 5-11: In the previous version of the manuscript, the only fitted parameter was 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 fit has been improved by fitting both parameters: K_{O_3} and k_{max}^I giving better coefficient regressions ($R^2=0.99$ and 0.83 for silica and XAD-4 particles, respectively). These changes have been included in the text and figures.

Technical comments: All references have been verified.

Table 1: The required details have been added in the table.

Figure 1: The inlet and outlet of the gas flow has been added. Reactor's dimensions have been added too.

Figure 4: The name of the regression line has been added. (This missing information was the consequence of the manuscript edition).

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S10866

ACPD

8, S10862–S10866, 2009

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