

We thank the referee for taking the time evaluating our manuscript. Please find below our response to each comment and corresponding text changes in bold-faced letters. The indicated page and line numbers refer to the online discussion paper.

The experiments have been performed using a newly developed irradiated rectangular channel flow reactor, operated at low pressure (2-4hPa). Under such conditions, I'm wondering how stable the organic films were? In fact, some of the compounds studied are still quite volatile and I would suspect some re-evaporation from the glass block in the reactor, was this observed? Could this lead to a redistribution of the organic film on other surfaces within the reactor – affecting the calculation of the uptake coefficient (leading to some underestimations)? Were the organic monitored using the CIMS? If re-evaporation occurred, then the film composition may not necessarily reflect the composition of the solution which was deposited on the glass block. Any comment on that?

We thank the referee for bringing up this point. The estimated vapour pressure of LEV is 2.0×10^{-4} (May et al., 2012). The vapour pressures NG and PP have not been obtained, but we assume that NG has a slightly higher vapour pressure than LEV and PP has a lower vapour pressure than LEV. The CIMS was operated in negative ion mode and thus we could not monitor potential volatilisation of organic molecules in parallel with the uptake experiments, although this is something we are aiming to achieve in future experiments. When calculating the mass loss due to evaporation only (Seinfeld and Pandis, 2006) using the vapour pressure of LEV (which has a similar molecular weight as NG), we estimate too much loss (similar to the total amount of organic material applied), which disagrees with our observations, i.e. the film did not visibly change for exposures of up to 1 hour at low pressures. Due to evaporation, a concentration profile establishes between the film surface and the cover of the I-RCFR, about 7 mm away. The characteristic time to establish this profile can be estimated by $t = l^2/4D$, where l is the height above the reactive surface and D is the diffusion coefficient (calculated using the Chapman-Enskog theory). This time is about 0.015 s, much faster than the mean residence time in the flow reactor of about 0.2 s. With this knowledge we can derive an evaporative flux given by (Cussler, 2010):

$$j = \sqrt{\frac{D}{\pi t}} (c_s - c_\infty)$$

where c_s is the concentration just at the reactive surface given by the vapour pressure, and c_∞ is the concentration at the top of the flow reactor which we assume to be zero, resulting in a conservative estimate. This yields an evaporative flux of $1.8 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$. For our experimental time scales and surface area of the organic substrate, we obtain a total loss of $\sim 2 \times 10^{-5} \text{ g}$ from the surface, which results in a $\sim 0.4\%$ loss of the total surface coverage over the course of the experiment. Since NG may possess a higher vapour pressure than LEV, we may expect a higher total loss from that substrate. This loss of mass seems to be reasonable, indicating only minor changes to the film surface, similar to observations of two other studies (Knopf et al., 2011; Slade and Knopf, 2013) where the films were kept under low pressure for longer time periods.

If the organic evaporates and recondenses downstream on other surfaces, the actual reactive surface area would increase resulting in an overestimation of the determined reactive uptake coefficient. However, evaporation and recondensation would be a

continuous process, also occurring before the initial exposure of the film to O₃. We determine the reaction kinetics in a comparative manner. This means, if reaction downstream occurs and does so in a relatively constant manner, derived reaction kinetics are not significantly affected as a result of employed technique. Furthermore, if this would be a significant effect, the likelihood to observe an increase in the O₃ signal after an initial decrease to a steady state value would be less likely. Lastly, in our previous study (Knopf et al., 2011) we expose similar films to low pressure for over one hour to reagents and do not observe complete volatilisation of the film (visually no difference is observed in film appearance). In some cases we also observe saturation after initial rapid uptake and thus an increase in the reagent ion signal. If the film would continuously evaporate and thus would reveal non-reacted surface sites, this behavior may not be observed. The above estimated evaporative flux suggests that during the 15 min experiment time for each data point, the composition of the film can change slightly. However, when looking at the PP/NG mixture under visible irradiation, we see a clear trend in the reactive uptake coefficient with amount of NG present. However, the referee is correct, that it could be that a similar percentage fraction of NG for each sample volatilised. We add the following sentence to section 2.5, page 7562, line 21:

“Evaporation of the organic substrate under the experimental conditions may be possible, but is assumed to be of minor importance according to estimations of the evaporative flux (Cussler, 2010). This is corroborated by visually insignificant changes of the organic substrates after an uptake experiment similar, to previous findings (Knopf et al., 2011; Slade and Knopf, 2013). Continuous evaporation of significant amounts of organic molecules may result in a continuous supply of unreacted surface sites, not supported by our findings of a LH type reaction mechanism described below.”

Low pressure should avoid important gas phase diffusion limitations. Nevertheless, it is mentioned that some corrections were applied to the data. How important were they?

The diffusion correction is on average < 15% for the measured uptake coefficients. We add the following information to section 3.2, page 7565, line 6:

“Correction for diffusion is on average < 15% for the measured uptake coefficients.”

It is mentioned that the surface somehow passivates upon reaction (leading to the determination of steady-state uptake coefficient, which is the correct parameter to report on). However, it is unclear to me how often the organic films were changed i.e., for each data point?

The organic films were changed for each pullback experiment, i.e., there was a fresh organic substrate for each data point. For the stepwise experiments, a fresh substrate was used at the beginning of the experiment, but was not changed for each stepwise increment. To make this point clearer we add the following sentence to section 2.2, page 7560, line 23:

“For each pullback experiment a freshly prepared organic substrate was applied. For the stepwise method, a fresh substrate was used at the beginning of the experiment, but was not changed for each stepwise increment during the experiment.”

In addition, we modify the following sentence on p. 7560, l. 21:

“At least 6 independent experiments, each using a fresh organic substrate, were conducted for each investigated species or mixture.” to

“At least 6 independent experiments were conducted for each investigated species or mixture.”

The pH of the solution is shown to affect the absorption spectrum of nitroguaiacol. Was therefore the pH effect on the photoenhanced uptake of ozone also studied? In this case, if I compared the output of the visible lamp to the NG absorption spectrum at pH=12, I could expect some photoenhancement, or am I wrong stating this? Please clarify in section 3.4.2 if those experiments were performed or not.

The pH effect on the photo-enhanced uptake of ozone was not studied. Although this would be a very interesting study, it cannot be accomplished under our experimental conditions since the nitroguaiacol is a solid film at these low pressures. However, in the atmosphere, nitroguaiacol may be in solution and pH effects would need to be considered. We will clarify this in section 2.6 since this is where we discuss the absorbance measurements. We add the following sentence to page 7563, line 3: “The effect of changing the solution pH on the uptake of O₃ was not explored in this study.”

The absence of photoenhancement under visible light for the PP/LEV mix is surprising to me. As pure PP exhibit photosensitizing properties, in the mix this compound should undergo competitive reactions with either O₃ or LEV, and therefore show some enhancement. Or was finally PP buried in LEV with no direct contact with incoming ozone?

This observation was surprising for the authors as well. Although the mean uptake value under VIS irradiation for 1:1 PP/LEV is higher than under dark conditions, the corresponding error is too large to definitively corroborate an enhancement. The referee may be correct that burial of PP in LEV could be the cause. In particular, since the burial of PP in LEV is not well controlled, this could explain the large value range. This point will be added to the text in section 3.4.2, page 7567, line 21 by modifying the following sentence:

“The addition of the PP photosensitiser to LEV does not yield an enhancement in O₃ uptake, within the experimental error.” changes to

“The addition of the PP photosensitiser to LEV yields a higher mean γ under VIS irradiation, however the uncertainty is too large to corroborate an enhancement. Since uptake of O₃ by pure PP is enhanced under VIS irradiation, γ of the PP/LEV substrate should be enhanced due to the presence of PP. However, PP may be buried within LEV thus hindering its photosensitising properties and making it inaccessible for reaction with O₃. Different levels of PP burial may explain the resulting range in uncertainty.”

We remove the following sentence from page 7567, line 22:

“Although LEV should be able to act as an electron donor and react with the triplet excited state of PP (Alvarez et al., 2012), it is not more readily able to adsorb or react with O₃.”

The uptake coefficients in the figures are given with arbitrary units (u.a.), this is not correct as the uptake coefficient is a dimensionless parameter. Please correct your figures.

We have corrected the figures according to the referee’s suggestion.

References

Cussler, E.L., 2010. Diffusion: Mass Transfer in Fluid Systems. Cambridge University Press, Cambridge.

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