

Interactive comment on “Substrate effects in the photoenhanced ozonation of pyrene” by S. A. Styler et al.

Anonymous Referee #1

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This manuscript describes experiments on ozonation of pyrene (Pyr) in different surface environments in the presence and absence of light. There is a modest enhancement of the rate of the decomposition of Pyr by ozone (O₃) in the presence of light, which is interpreted as a result of reactions between the excited state pyrene (Pyr*) molecules and O₃. The most interesting result of this paper is observation of two competing mechanisms, one involving reactions of Pyr* with adsorbed O₃ and the other involving reactions with gas-phase O₃. The mechanisms can be distinguished because the former follows a Langmuir-Hinshelwood dependence on the gas phase ozone concentration, and the latter is linear in [O₃]_g. Parallel quenching of Pyr* by oxygen and other molecules is going on in parallel; it is not believed to result in the Pyr decomposition in the absence of O₃. The mechanism is summarized in Scheme 1.

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The paper is well written, the experiments are solid, and the conclusions are supported by extensive literature citations. ACP is an appropriate journal for the paper on this topic. It can therefore be published in ACP after minor revisions. I have the following comments:

On page 27828, the authors state that oxidation of PAH in films may have implications for human health. I do not think it is likely as in most cases the oxidation products remain in the film and therefore cannot easily come in direct contact with humans. Is there evidence of significant health effects through skin contact with urban surfaces?

On page 27830, I would replace “5X” by “5 times”. Same comment applies to Fig. 3 caption.

On page 27834, the authors state that “At the surface of a more dilute pyrene solution, the same dependence upon ozone concentration was observed.” There is no evidence to support this statement in Figure 3. There is just one point measured at a lower concentration - not enough to infer the dependence.

I found the discussion of the mechanism R1-R6 on page 27840 and the statement “We attribute this change in mechanism to an increased favourability of A-type pathways at the highly polar air-aqueous interface.” too qualitative. I would prefer to see this mechanism contrasted with the Langmuir-Hinshelwood for the illuminated as well as dark oxidation so that the differences these mechanisms can be better emphasized.

Finally, can the authors rule out the possibility that Langmuir-Hinshelwood still applies at the aqueous illuminated surface but the parameter B is increased significantly?

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