

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

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We thank the reviewer for the interesting comments. Below, we address each in turn.

Comment: My main concerns are related to the high ozone concentrations applied to these experiments. To my opinion the ozone concentrations are extremely high i.e. higher than 100 ppm and thus not realistic. Why the authors did not work with lower ozone concentrations? Is it an experimental limitation?

Response: Our ozone concentrations, which are indeed significantly higher than those present in the atmosphere, are nonetheless comparable to those previously used in a number of similar studies (see e.g. (Kwamena et al., 2006; Kahan et al., 2006; Kahan and Donaldson, 2008; Mmereki and Donaldson, 2003)), which together have provided

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valuable information regarding the mechanisms of heterogeneous oxidative processes. The “saturation regime” observed in these experiments at high gas-phase ozone concentrations, for example, has provided confirmation that the heterogeneous ozonation of a variety of condensed-phase species on a number of atmospherically relevant substrates proceeds via a Langmuir–Hinshelwood (L–H) surface-mediated mechanism. In a number of cases, we have used the L–H parameters obtained in high-concentration studies to assess the significance of reactive pathways at more atmospherically relevant ozone concentrations (see e.g. (Kahan et al., 2006)). Work by Clifford et al. (Clifford et al., 2008), which investigated the uptake of ozone by chlorophyll at aqueous surfaces from both the surface and gas-phase perspectives, suggests that this is not unreasonable: nearly identical ozone uptake parameters were observed for experiments monitoring chlorophyll loss at the surface and uptake of gas-phase ozone by the surface, despite the fact that the former experiments were performed at ozone concentrations orders of magnitude greater than the latter. Recently, our group worked collaboratively to study the ozonation of solid pyrene films from both the surface and gas-phase perspectives (Styler et al., 2009). Although these two sets of experiments were performed in entirely different concentration regimes, their results were comparable under dark conditions. Moreover, under light conditions, the divergent results of these experiments arose primarily through the existence of different photochemical loss pathways for ozone and pyrene rather than from the different gas-phase ozone concentrations employed.

Comment: Figure 3A shows the Langmuir–Hinshelwood dependence on ozone concentrations under dark and in presence of light. In this Figure it can be seen that basically the surface is saturated in a whole range of applied ozone concentrations. I think that Figure 3a does not show an evident photoenhancement as the authors claimed in the text. The two data sets i.e., ozonolysis under dark and in presence of light are basically the same within the experimental errors. Precisely, the difference in the obtained rate constants is only factor of two at the whole range of applied ozone concentrations. Can the authors elucidate this in more details? It looks like that slight difference be-

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tween the two data sets may be attributed to the evaporative loss of pyrene under light irradiation of the solid pyrene surface.

Response: While the observed photoenhancement is indeed modest, we do believe it significant: as shown in Table 1, the pseudo-first-order rate constant k_{obs} for the ozonation of solid-film pyrene increased from 2.44 ± 0.92 to 4.71 ± 0.81 upon illumination at an ozone concentration of $\sim 6 \times 10^{15}$ molecules cm^{-3} . We do not agree that the enhanced loss of pyrene upon illumination can be attributed solely to evaporative loss. As noted in the manuscript, the illumination of solid pyrene films in the absence of ozone led to a slow, linear decrease in pyrene fluorescence intensity; this evaporative loss continued until no fluorescence was observed (~ 1 – 2 h). Upon illumination in the presence of ozone, by contrast, a rapid, exponential loss of pyrene was observed—after ~ 15 minutes, a significant and constant residual fluorescence remained. These results suggest that the formation of a surface layer of non-volatile ozonation products served to prevent evaporative loss of pyrene from the solid film.

Comment: Concerning the experiments under dark conditions in Figure 3b the curve is forced to pass through zero otherwise all data points can be well fitted with linear regression line. Perhaps, some experimental points in the range of ozone concentrations between 0 and 1.8×10^{15} molecules cm^{-3} could clarify this dilemma.

Response: Under dark conditions in the absence of ozone, pyrene could be lost from the aqueous surface only via bulk dissolution or evaporation. Our experimental protocol involves a baseline-recording period of 5–10 minutes prior to the introduction of ozone; during this time period, no significant loss of pyrene was observed. Given this observation, it seems reasonable for the curve to pass through the origin. Our results at the aqueous surface under dark conditions are essentially identical to those reported by Donaldson et al. (Donaldson et al., 2005) for pyrene at the aqueous surface over a broader range of ozone concentrations, which clearly suggest that this reaction proceeds via a L–H mechanism. This fact, coupled with observations of L–H kinetics for the reactions of gas phase ozone with anthracene, (Mmereki et al., 2004) chlorophyll

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(Clifford et al., 2008) and other compounds at the air–aqueous interface suggests that our inference of L–H kinetics is reasonable.

Comment: In addition to the kinetic data for the future I would strongly recommend product study of this heterogeneous reaction under dark conditions and in presence of light in order to shed some light on the reaction mechanism.

Response: Work in this area to date has shown that the products of pyrene ozonation are highly medium-dependent: while the dark ozonation of pyrene in aqueous solution has been shown to yield fourteen products, including a variety of substituted phenanthrenes and biphenyl-type oxidation products (Yao et al., 1998), the ozonation of azelaic acid-sorbed pyrene has been shown to yield only two main products (Gao et al., 2009). While beyond the scope of the current study, we do agree that these studies would be useful in future.

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