Atmos. Chem. Phys. Discuss., 10, C12268–C12269, 2011
www.atmos-chem-phys-discuss.net/10/C12268/2011/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 12 January 2011

This article presents the heterogeneous reaction of ozone on solid pyrene films and pyrene adsorbed at air-octanol and air-aqueous interfaces and the possible role of photoenhancement in this reaction. Under dark conditions and upon near-UV illumination of the solid pyrene surface, the first order rate constants depend inversely on the O3(g) concentration, implying a Langmuir-Hinshelwood kinetic mechanism. On the other hand, the heterogeneous ozonolysis of pyrene at the air-aqueous interface exhibits Langmuir-Hinshelwood kinetic mechanism whereas under solar irradiation the first order constants depend linearly with the ozone concentrations. The manuscript is well written, consistent and the obtained results follows the pattern of the previous work (Styler et al., 2009) done by group of Donaldson. In fact, these results represent the continuation of the efforts of Donaldson's group to strengthen the knowledge of an emerging topic such as light induced heterogeneous chemistry. I recommend publica-

tion of this article in the Atmospheric Chemistry and Physics after satisfying answers of my questions stated below.

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. Figure 3A shows the Langmuir-Hinschelwood 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 between the two data sets may be attributed to the evaporative loss of pyrene under light irradiation of the solid pyrene surface. Why the authors did not work with lower ozone concentrations? Is it an experimental limitation? 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/cm3 could clarify this dilemma.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 27825, 2010.