

Interactive comment on “Heterogeneous photochemistry of imidazole-2-carboxaldehyde: HO₂ radical formation and aerosol growth” by L. González Palacios et al.

Anonymous Referee #1

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This is a nice manuscript that should be of great interest to the atmospheric community. HO₂ production from aerosols has not been widely investigated; this work suggests that it should not be ignored. I recommend that this manuscript be published following some minor revisions and clarifications.

Major comments:

Is the reaction occurring only at the surface, or also in the bulk? Did PHO₂ depend at all on film thickness? If only the surface reaction matters, then bulk phase diffusion (and reactions) can be ignored. If production in the bulk is important, I would expect HO₂ production to depend on film thickness. Did it?

C1

What is the expected extent of light attenuation throughout the film? If light is attenuated by the film, photolysis in CWFT experiments would occur primarily at the glass-film interface, and any HO₂ formed would have to diffuse to the surface before being released to the gas phase. Conversely, photolysis in the aerosol flow tube would occur primarily at the aerosol-air interface, and no diffusion would be required prior to HO₂ desorption to the gas phase. Could this explain the greater gas-phase HO₂ production in the aerosol flowtube compared to in the CWFT (either in addition to or in place of increased surface area of the aerosols)?

In the Conclusion the authors state that HO₂ production is reduced at dry film surfaces due to increased viscosity (and therefore decreased IC and HO₂ mobility) within the film. Is it possible that the reactions occur at the surface and are enhanced by the presence of water? At what RH is a monolayer of water expected to exist at the film surface? Could ionized citric acid behave differently than molecular CA?

Minor Comments: Equation 1 uses 300 nm as a lower limit. Is this appropriate? Is light at that wavelength absorbed by the jacketed flow tube? Even a small change in the wavelength limits could change the calculated photon flux significantly.

Equation 1 also bases the absorption cross section of IC on that measured in aqueous solution. Is the absorbance of IC in a solid film expected to be the same as that in aqueous solution?

There is only one data point at O₂ levels greater than 55% shown in Figure 6. I would feel more comfortable with the stated conclusion that HO₂ production decreases above 55% O₂ with more measurements at higher O₂ fractions.

p. 4 lines 103-106: "... that in absence of other known radical sources confirm that HO₂ production from aerosols can start photochemistry." I don't understand what this sentence means. Doesn't photochemistry form the HO₂?

p.7 line 182-183: What do you mean by a "thin" film? Be a bit more quantitative.

C2

p. 11 line 303: "Each data point was measured from a freshly prepared coated film in the flow tube." What is meant by "each data point"? Figure 2 is a time series; presumably each data point was acquired during the same experiment (using the same film).

p. 13 line 365: In describing Figure 6, the authors say that "A marginal decrease below 15% O₂..." Marginal might not be the most appropriate term, since HO₂ production decreases to zero in the absence of O₂.

p. 18 line 508 -510: OH does not start Fenton reactions. Please reword.

Figure 4: What are the open circles in the plot?

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