

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

Anonymous Referee #2

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The work by González Palacios et al. provides indirect evidence for the formation of HO₂ during photosensitized reactions of aerosols and thin surface films containing an imidazole and a H-atom donor (e.g., citric acid or limonene). This is a complicated system. The results are of high quality and appropriate methods and techniques were applied to the problem. I recommend publishing after the following points are addressed.

It was not clear how the data support that this reaction is autocatalytic? Are not autocatalytic processes characterized by a logistic product profile, whereas the NO₂ vs time profile shown in Figure 2 show NO₂ formed decreasing between 20 and 75 minutes. Is there any indication that this will level off at some significant steady state at

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later reaction times? On line 296-299 the authors state that the system only slowly evolves into a steady state; however how long does that take? If it does not reach steady-state, and the system ceases to convert NO into NO₂ over time, then this is not an autocatalytic system.

The paragraph starting on Line 70 explains the motivation behind studying imidazole photochemistry. As stated by the authors, imidazole is thought to be generated from the reaction of glyoxal with ammonium and amines. The authors only discuss imidazole in SOA has been strictly in laboratory settings (see references cited), which may or may not be reflective of the real environment. I feel this section should include current views (for and against) on the importance of imidazole in atmospheric samples. The recent article by Teich et al. (ES&T 2016, 50, 1166) may be of help here. Such a discussion will help to better convey the atmospheric significance of this study.

Did the authors determine the concentration of nitrate present in their coatings during or following their reactions? When such high levels of NO_x, it may be possible that some nitrate could be deposited to the surface. In such a case, photolysis of nitrate could release NO₂ into the gas phase. Also, what was the pH of the films coating the glass walls? If citric acid was used this could have lowered the coating pH, in which case one must consider acid-base chemistry as well. This could impact organic photochemical reaction intermediates and also the yield of HO₂, NO₂ (via nitrate photolysis) and HONO generated in the system.

In the case of the aerosol flow reactor, citric acid was not used; Limonene was used instead, which would not acidify the particle. This represents a major difference between the CWFT and aerosol flowtube measurements that was not discussed. I would be interested in seeing if the authors think this difference could explain why NO_x consumption in the aerosol system was so different than during the CWFT experiments.

line 40. The phrase, "...implications consist in a..." is awkwardly phrased. Perhaps revise to say rather: "Our results indicate a potentially relevant contribution..."

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line 58. Include “concentrations” after OH2

lines 83-84: Paragraph too long. I suggest inserting a paragraph break between these lines

lines 128-134: It appears that J-values for NO₂ photolysis were calculated using clean flow tubes (i.e., in the absence of a coating). Therefore, one is assuming that the J-values for the clean tube are the same as those for a coated tube. Does the IC coating on the coated-wall flow tube attenuate the light enough to invalidate this assumption? If the IC coating does attenuate the light transmitted through the flowtube, how could this bias interpretation of the results?

line 253 (and other places where the term “H-donor” is used): The authors might want to clarify that the VOCs are H-atom donors, rather than proton donors as in the case of a Bronsted acid.

lines 314-318: It is not clear to me: Do the authors think that the NO to NO₂ conversion by HO₂ is occurring in the organic surface film or in the gas phase? How can they be sure?

lines 319-323: The concentration of citric acid [CA] is in such excess relative to the imidazole. Could it not be assumed that [CA] is constant over the course of the experiments? In that case, why not just plot [HO₂] vs [IC] instead of vs [IC]x[CA].

lines 344-347: The authors discuss the role of coating viscosity on photochemistry. A recent article by Hinks et al. (PCCP, 2015, DOI: 10.1039/c5cp05226b) discusses this effect nicely and should be cited here.

line 361: Cannot also H₂O photophysically quench the triplet excited state? Is this important for this system?

lines 403-406: The authors mention that the photosensitizer 4-BBA behaves similar to IC. I would like to see this data included in the SI.

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lines 426: With respect to ozone formation in the flowtube and aerosol systems, did the authors measure ozone and can they confirm that it was not observed in the system? Lifetimes of ozone were indicated for these experiments, do they account for heterogeneous loss as well?

Figure 8: Focusing on the “IM-C-OH(dot)” intermediate, should not the dot be centered on the carbon and not the alcohol H?

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