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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Halogen activation and radical cycling initiated by imidazole-2-carboxaldehyde photochemistry" *by* Pablo Corral Arroyo et al.

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Below, we provide a point-by-point response to the comments raised by reviewer 2.

Reviewer: This is a nice contribution aiming at understanding how triplet states chemistry may induce both halogen activation and HO2 release. Imidazole-2-carboxaldehyde (IC) was used a proxy for chromophoric dissolved organic matter (CDOM) or brown carbon (BrC) in coated wall flow tube experiments. Its chemistry was simulated by a simple "box" model, which was adjusted to the measured yields. The experiments and calculations are performed according to the current best standards. While the manuscript itself is well written, it could nevertheless benefit from

some reediting as some sentences are repeating between the experimental and result sections. This manuscript is definitively suitable for publication in Atmospheric Chemistry and Physics, and I would raise only a very few minor comments.

Response: We would like to thank the reviewer for this positive assessment. We agree with the comment regarding the language, and accordingly we will provide a thorough check of the language and consider some streamlining of parts of the text and remove redundancy among the different sections in the revised version.

Reviewer: While the films were prepared from aqueous solutions, it unclear from the experimental section if those stay liquid during the experiments or if they were drying out. The authors should make clear in which phase the experiments were performed. There is only a few superficial mention about the relative humidity set during the experiments, which may affect both the phase and temperature of the films.

Response: Comment well taken: While we have characterized citric acid coatings in the cited previous studies in more detail, this has not been clearly enough described here. Therefore, we will include the following sentence in the experimental description: "Since films were never dried below 35 % RH, they are expected to remain concentrated liquid aqueous solutions at 35 % RH with a viscosity around 10 - 100 Pa s."

Reviewer: In order to adjust to the measurements, the authors decided to keep the inter-halogen conversion reactions (reactions 8-11) at their literature values and tune the HO2 scavenging reactions 12 – 16 (or 11-15 as stated elsewhere in the text). To obtain reasonable model results, they were reduced. Here as I wondering if the authors have thoughts on the possible influence of the CA. radicals produced in reaction R4? Very recently, Roveretto et al (ACS Earth Space Chem., 2019, 3 (3), pp 329–334) reported, in similar experiments, between those organic and inorganic radicals. While this is not affecting the conclusions made here, it might explain the need of adjusting part of the rate constants in Table 1.

Response: Agreed. We will include the following sentence in the results section: "CA

daughter radicals can react with halide radicals and produce halogen-containing organic compounds, as already observed in aquatic media (Roveretto et al., 2019). This can result in a partial scavenging of the halide radicals and it might be an explanation for the need to decrease the rate coefficients for R11 to R15."

References

Roveretto, M., Li, M., Hayeck, N., Brüggemann, M., Emmelin, C., Perrier, S., and George, C.: Real-Time Detection of Gas-Phase Organohalogens from Aqueous Photochemistry Using Orbitrap Mass Spectrometry, ACS Earth and Space Chemistry, 3, 329-334, 10.1021/acsearthspacechem.8b00209, 2019.

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