Dear editor

In response to the review comments, we have first implemented the changes as announced in our response to the review comments in ACPD. Then, we have substantially improved the narrative of the text, text flow and structure and English grammar, which required quite some moving around within the individual sections, but no change to the overall structure. A few more minor changes in the presentation of the implications have been done, which are described after the actions resulting from the review comments. At the end of this document, the manuscript in track changes mode is appended.

Below we repeat the comments (plain), our response (bold) and the actual action in the revised version (italics),

Reviewer 1:

- Please comment about the importance of differences between the spectra lamps and radiation in the atmosphere and possible implications for this study and atmospheric implications.

Thank you for this comment. We will include the following text in the conclusion:
"At 0◦ zenith angle the ratio of the excitation rates of IC by sunlight (spectrum given in Figure S1) and that by the lamps used in our experiments (j_{sun}/j_{lamps}) is about 2.83. Therefore, in terms of irradiation our results can be extrapolated to the atmosphere with confidence."

Final action in text: We have added the following sentence to the conclusions on line 11 of page 11: "We note that at 0° zenith angle, the solar actinic flux is about 3 times greater than the UV lamps we used in the experiment, and thus excitation rates of IC may be 3 times faster than what was used here."

- Some comments should be added related the possible effect of Cl- in the mechanism proposed since in sea salt aerosols Cl- is going to be present.

Thank you this comment. We will include the following text in the conclusion:

"Assessment of chlorine activation via IC as chromophore and sensitizer reacting with chloride, which is present in higher concentrations in sea salt aerosol particles (~5.4 M) (Herrmann et al., 2003), was beyond the scope of this study. While the ratio of chloride to bromide or iodide is higher than the inverse ratio of the corresponding rate coefficients (Tinel et al., 2014), the complex radical chemistry and kinetics requires detailed attention to understand impacts on chlorine activation and photosensitized HO_2 production."

Final action in text: We have added the following sentence to the conclusions at the bottom/top of pages 9/10: "Assessment of chlorine activation via IC as chromophore and sensitizer reacting with chloride, which is present in higher concentrations in sea salt aerosol particles (~5.4 M) (Herrmann et al., 2003), was beyond the scope of this study. While the ratio of chloride to bromide or iodide is higher than the inverse ratio of the corresponding rate coefficients (Tinel et al., 2014), the complex radical chemistry and kinetics require detailed attention to understand impacts on chlorine activation and photosensitized HO_2 production."

- This sentence need to be finished up: "Code and data availability. The data for simulations

Yes, of course, we will deposit the data underlying each figure in the supporting material, and adapt this statement accordingly in the revised version.

Final action in text: The code and data availability statement now reads: "The data underlying Figures 2 and 3 and the matlab codes of the steady-state model calculations are available as supporting files."

Reviewer 2

…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.

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.

Final action in text: As mentioned above, we have substantially edited the whole manuscript again to improve text flow, conciseness and English language. A few specific important changes on top of that will be mentioned at the end of this description of revisions.

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.

We agree with this comment. 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."

Final action in text: "Once prepared, a solution was deposited in the glass tube while rolling and turning the tube in all directions at room temperature under a gentle flow of N_2 humidified to the RH later used in experiments. This procedure was necessary to ensure homogeneous thin films checked by visual inspection and to prevent the film from drying out prior to the experiments…. Films are expected to be liquid at 35 % RH and have a viscosity of 10 - 100 Pa s (Song et al., 2016)."

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.

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)."

Final action in text: We have added a citation to Roveretto et al. (2019) in the introduction section on page 3, line 25, where such processes are mentioned at the general level. In section 3.1, page 8, line 13, we have added: "This can be explained if CA derived radicals reacted with halogen radicals to produce halogen-containing organic compounds, as already observed in aquatic media (Roveretto et al., 2019), which could result in a partial scavenging of halogens. " Then, in the iodine activation section 3.2, on page 9, line 1, we have added: "Alternatively, sinks of halides in the films could be the reaction of halide radicals ($I^{\bullet}$ or I_2^-) and of HOI or HOBr with organics producing Org-X (Abrahamsson et al., 2018; Gilbert et al., 1988; Roveretto et al., 2019) or further oxidation of iodine to iodate, which was beyond the scope of our study."

Further changes to the manuscript

The discussion of the model application on page 7 has been improved to better represent the differences between model output and measurements.

We noticed an error in reporting the model prediction for iodine release for the initial film conditions, which is in fact much higher than what was actually measured, on page 7, line 27. This is reasonable, because the measurement cannot resolve a sharp initial release of iodine: "The maximum of the iodine release was 5.5×10^{13} molecules min^{-1} cm^{-2}. When normalized to the initial amount of iodide present in the film, this corresponds to a iodide life-time of around 8400 s, thus a bit more than 2 hours. The steady-state model prediction is 4.9×10^{15} molecules min^{-1} cm^{-2} at the initial concentration of iodide, which cannot be directly compared to the measurement, because the measurement with the SMPS could not resolve a sharp initial release. Note in addition that the model is not following the system over time." We refrain from further speculating on model uncertainty at this point in the text, since this is discussed in the previous section.

In the previous manuscript version, we have only used the simple back-of-the-envelope calculation made in the introduction section about iodide oxidation by triplet excited states to compare to iodide oxidation rates induced by ozone, thus without actually using the results of the present study. We therefore added the results of a few additional model estimates based on the present study: "Based on the results obtained, we can refine this number. We note that the experiment in Figure 3 cannot be directly extrapolated to atmospheric conditions due to the high 33 mM iodide concentration used, which suppresses the triplet concentration to 10^{-12} M. In addition, the viscous films were 3.4 µm thick, thus beyond atmospheric particle size ranges. We therefore run model calculations with 10^{-6} M iodide, a film thickness of 0.5 µm and with the IC concentration adjusted such that the triplet

concentration at steady state reached 10^{-10} M. Under these conditions, the iodine release is estimated at 4.1×10^{-7} M s^{-1} at 35% RH and roughly a factor of 2 larger when the diffusion coefficients are set to the 10^{-6} cm^2 s^{-1} range for a low viscosity liquid." This allowed to sharpen the conclusion. The numbers have also been updated in the abstract.

We corrected equation (2) by a factor 2, since it refers to O_3 uptake (and thus iodide, I^-, oxidation), and not I_2 release.

Halogen activation and radical cycling initiated by imidazole-2-carboxaldehyde photochemistry

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Abstract. Atmospheric aerosol particles can contain light absorbing organic compounds, also referred to as brown carbon (BrC). The ocean surface and sea spray aerosol particles can contain light absorbing organic species referred to as chromophoric dissolved organic matter (CDOM). Many BrC or CDOM species ~~(especially~~can contain carbonyls, dicarbonyls or aromatic carbonyls such as imidazole-2-carboxaldehyde (IC)~~)~~, ~~and are referred to~~which may act as photosensitizers because they form triplet excited states upon UV-VIS light absorption. These triplet excited states are strong oxidants and may initiate catalytic radical reaction cycles within and at the surface of atmospheric aerosol particles, therefore increasing the production of condensed phase reactive oxygen species (ROS). Triplet states or ROS can also react with halides generating halogen radicals and molecular halogen~~s~~ compounds. In particular, molecular halogens can be released into the gas phase, one pathway of ~~and may contribute to~~ halogen activation. In this work, we studied the influence of bromide and iodide on the photosensitized production and release of hydroperoxy radicals (HO_2~~.~~) upon UV irradiation of films in a coated wall flow tube (CWFT) containing IC in a matrix of citric acid (CA) irradiated with UV light. In addition, we measured the iodine release upon irradiation of IC/CA films in the CWFT. We ~~used~~ developed a kinetic model coupling photosensitized CA oxidation with condensed phase halogen chemistry to support data analysis and assessment of atmospheric implications in terms of HO_2 production and halogen release in sea-spray particles. As indicated by the experimental results and confirmed by the model, significant recycling of halogen species occurred via scavenging reactions with HO_2~~,~~ ~~and~~ These prevented the full and immediate release of the molecular halogen (bromine and iodine) produced~~, while the HO_x chemistry was partially shut down~~. ~~The~~ R~~r~~ecycling ~~efficiency is~~was ~~affected~~ stronger ~~by~~ at low relative humidity, attributed to diffusion limitations ~~and is found to be higher at low relative humidity~~. Our findings also show that the HO_2 production from BrC or CDOM photosensitized reactions can increase due to the presence of halides, leading to high HO_2 turnover, in spite of low release due to the scavenging reactions. We estimated the iodine production within sea salt aerosol particles due to iodide oxidation by ozone at 5.0~~9~~ × 10^{-6}~~5~~ M s^{-1} assuming ozone was in Henry's Law equilibr~~i~~~~r~~um with the particle. However, using an ozone diffusion coefficient of

10^{-12} cm^2 s^{-1}, iodine activation ~~can drop several orders of magnitude~~ in an aged, organic-rich sea-spray derived aerosol to 5.5~~1.1~~ × 10^{-8}~~7~~ M s^{-1}. The estimated iodine production from BrC photochemistry based on the results reported here amounts to 2.5~~4.01~~ × 10^{-7} M s^{-1} and indicates that BrC photochemistry can exceed O_3 reactive uptake in controlling the rates of iodine activation from sea spray particles under dry or cold conditions where diffusion is slow within particles.

1 Introduction

Volatile halogen-containing species such as CH_3X, CH_2XY, HOX, XY, and X_2 (where X and Y can be Cl, Br and I) are known as activated halogen species (AHS)~~.,~~ ~~and~~ They are produced at the ocean surface, in snowpacks or in aerosol particles and emitted into the atmospheric gas phase. ~~and~~ ~~T~~their production is referred to as halogen activation. ~~The production of AHS~~Halogen activation is driven by oxidation of halides by ozone (Carpenter et al., 2013) ~~(~~Schmidt et al., 2016) ~~or by~~and radicals (e.g., OH or NO_3 ~~for example~~) (Sander and Crutzen, 1996), N_2O_5 (Behnke et al., 1997)~~(add citation)~~ or photochemical oxidation (Wang and Pratt, 2017;Wren et al., 2013). These volatile compounds can also be em~~m~~itted to the atmosphere ~~by~~ in the form of biogenic ~~emissions of~~ halogen-containing organic species (Org-X) (Hepach et al., 2016;Vogt et al., 1999), or by volcanos, among other processes (Simpson et al., 2015). AHS are precursors of reactive halogen species (RHS) such as X atom or XO (Sherwen et al., 2016a), which ~~trigger~~ affect oxidative processes in the gas phase (Saiz-Lopez et al., 2012). In the troposphere, for example, the presence of RHS shifts the HO_x equilibrium (HO_2 ↔ OH) towards OH (Bloss et al., 2005;Chameides and Davis, 1980;von Glasow et al., 2004;Saiz-Lopez, 2012;Sommariva et al., 2012;Lary, 1996), especially for the case of IO (Schmidt et al., 2016;Stone et al., 2018;Saiz-Lopez et al., 2008;Bloss et al., 2005;Dix et al., 2013;Volkamer et al., 2015). RHS also influence the budgets of nitrogen oxides (NO_x), organic compounds and organic peroxy radicals (Simpson et al., 2015). It has been observed that RHS of iodine produce ultrafine particles found in coastal areas (McFiggans et al., 2010;Mahajan et al., 2011). This new particle formation occurs via polymerization of I_2O_5 or HIO_3 (Hoffmann et al., 2001;McFiggans et al., 2004;Saunders and Plane, 2006;Sherwen et al., 2016b;Sipila et al., 2016), which ~~is~~ are produced by the (photo)oxidation of iodine precursor species such as I_2 (Saiz-Lopez and Plane, 2004), HOI (Carpenter et al., 2013;Sherwen et al., 2016b) and Org-X (Carpenter, 2003). The production and cycling of AHS and RHS at the ocean surface or in sea-spray particles are key processes to understand their release into the gas phase and the contributions to their emission fluxes (Pechtl et al., 2007;Carpenter et al., 2013;Herrmann et al., 2003).

~~Photochemistry can trigger many oxidative processes in the atmosphere which contribute directly to the oxidative budget both in the condensed and gas phases of the atmosphere, by producing oxidizing excited molecular states and radicals such as triplet states, singlet oxygen or HO_x radicals~~ (Canonica, 2000;George et al., 2015)~~. Brown carbon (BrC) is defined as the fraction of organic compounds in atmospheric aerosol particles that absorbs efficiently in the UVA-VIS range. Some BrC species can undergo direct photolysis, while others~~

Apart from O_3, N_2O_5 and inorganic radicals, ~~Halogen~~ halogen activation can also be initiated by triplet excited states of light absorbing organic compounds (Tinel et al., 2014;Jammoul et al., 2009). Typically referred to as brown carbon (BrC)(Laskin et al., 2015)~~)(cite Laskin), Oo~~rganic compounds absorbing in the UVA-VIS range are ubiquitously present in atmospheric aerosols ~~and are then referred to as brown carbon (BrC)(cite Laskin)~~. Similar compounds also occur in marine or terrestrial water environments, there referred to as chromophoric dissolved organic matter (CDOM). The involvement of triplet forming CDOM or BrC species, also termed photosensitizers, in ~~influenced by photosensitizing species, which can photocatalyze~~ radical chain ~~reactions~~ oxidation and redox processes characterized by the interplay of organic radicals and reactive oxygen species (ROS) have first been recognized in aquatic photochemistry (Canonica, 2000;McNeill and Canonica, 2016)~~(cite Canonica; cite McNeill review)~~ and since recently also in atmospheric aerosol photochemistry (George et al., 2015)~~(cite George 2015). involving e.g., organic and HO_x radials via excited triplet states. Some species of organic matter that absorb UV and visible light, referred to as brown carbon (BrC), can be photosensitizers and has previously shown to oxidize halides~~ (Tinel et al., 2014) ~~and preceed halide radical chemistry at the sea water surface (Jammoul et al., 2009). Likely, halide radical chemistry also occurs in sea spray aerosol particles, and contributes to halogen activation in the atmosphere. We note that in oceans and terrestrial waters, colored dissolved organic matter (CDOM) is another term to refer to light absorbing organic matter.~~

~~Even though quantification of the triplet forming species in aerosol particles is still in its infancy (Kaur and Anastasio, 2018), the~~ ~~Typical p~~Photosensitizers of atmospheric interest absorb above 300 nm and typically ~~are~~have carbonyl~~s,~~ functions ~~which absorb above 300 nm especially when~~ attached to an aromatic system (see absorption spectra in SI Fig~~ure~~. S1) (Canonica, 2000). Aromatic carbonyls may derive from oxidation of aromatic (and phenolic) compounds in the atmosphere. They may also derive from multiphase chemistry of carbonyls in aqueous ammonium sulfate (AS) aerosol, as is the case for imidazole-2-carboxaldehyde (IC) derived from glyoxal, which is a globally important oxygenated volatile organic compound (OVOC) from biogenic VOC oxidation (Stavrakou et al., 2009). IC (absorption spectrum in Fig. S1) ~~was reported being an active~~is ~~also~~ an important photosensitizer ~~aerosols~~ (Aregahegn et al., 2013;Kampf et al., 2012;Yu et al., 2014)~~.Imidazole-2-carboxyldehyde (IC) is a BrC proxy (absorption spectrum in Fig. S1) and well-known photosensitizer~~ (Corral-Arroyo et al., 2018;González Palacios et al., 2016) and is used as a proxy in the present study.

The concentration of ~~organic matter and potential chromophores~~photosensitizing BrC or CDOM species in marine and continental aerosol particles is high enough to represent a substantial source of~~be sufficient as precursors for~~ triplets ~~are is significant in marine aerosol particles~~ (O'Dowd and de Leeuw, 2007;Blanchard, 1964;Hoffman and Duce, 1976;Hunter and Liss, 1977;Cincinelli et al., 2001;Chen et al., 2016)~~.~~. ~~but~~When BrC is derived from ~~also in continental aerosol particles, especially when deriving from bb~~iomass burning, its concentration is especially high (see review by Laskin et al. (Laskin et al., 2015)~~(cite)~~. ~~Clearly, H~~halides are internally mixed with organics in continental aerosol particles originating from long-range transport or local sources and in marine environments at the ocean surface or in sea-spray aerosol (Knopf et al., 2014). In absence of direct measurements of excited triplet states in aerosols related to these environments, we may consider ~~From~~ the steady-state concentration of triplet states in fog water of up to 10^{-13} M reported by Kaur and Anastasio (Kaur and Anastasio,

2018). Assuming that drying of such fog droplets leads to representative triplet concentrations in general, the upper limit of the concentration of triplet states in aerosol particles would be around 10^{-10} M due to concentration at the lower water activity. The concentration of halides iodide and bromide in sea spay aerosol particles may reach 10^{-6} M for iodide (Pechtl et al., 2007;Baker, 2004, 2005) and 8×10^{-3} M for bromide (Herrmann et al., 2003), respectively. Assuming Using the concentration above and a rate coefficient of the reaction between a typical sensitizer triplet state and iodide of 5×10^{9} M^{-1} s^{-1} (Tinel et al., 2014), we calculate that iodine activation may reach 2.5×10^{-7} M s^{-1}, which In absence of diffusion limitations, this leads to a low short life reactive time lifetime on the order of seconds for iodide in the aqueous phase. De Laurentiis and co-workers suggested that excited triplet states can could oxidize bromide faster than OH radicals in sea water seawater (De Laurentiis et al., 2012). Some modelling studies of aerosol chemistry consider halogen chemistry driven entirely by inorganic halogen chemistry to be important (Sherwen et al., 2016b;Sherwen et al., 2016a). while Although, Pechtl et al. claimed that reactions with dissolved organic matter may be included as a relevant HOI deactivation pathway (Sarwar et al., 2016;Pechtl et al., 2007;Roveretto et al., 2019). The contribution of p Photosensitized halogen activation is less understood and is missing has not been included in these models. This indicates that photosensitized chemistry may contribute significantly to the halogen activation in sea spray particles.

Typical photosensitizers of interest are carbonyls, which absorb above 300 nm especially when attached to an aromatic system (see absorption spectra in SI Figure S1) (Canonica, 2000). In more detail, Figure 1 illustrates the catalytic cycle of a photosensitizer in an organic aerosol particle in presence of halides. First, the photosensitizer (P) absorbs radiation. This is followed by singlet (P*(s)) to triplet (P*(t)) intersystem crossing. The triplet state is long lived and acts as an oxidant (Canonica, 2000) reacting with an electron donor, e.q. a halide ion (X^-) or an organic H atom donor, producing a ketyl radical ($PH^{\bullet}/P^{\bullet-}$). Oxygen competes with electron/H atom donors for the triplet being able to produce singlet oxygen ($^1O_2$) from its reaction with the triplet. The ketyl radical passes on an electron or hydrogen atom to oxygen or another electron acceptor (e.g., NO_2 (Stemmler et al., 2006)) producing HO_2 and returning the photosensitizer to its initial ground state. The efficiency of the catalytic cycle quantum yield in terms of oxidation of an electron donor and reduction of electron acceptor (e.g., formation of HO_2) per absorbed photon is reduced affected by competing processes, such as the deactivation of the singlet, deactivation of the triplet (phosphorescence, non-radiative decay and reaction with oxygen) and other radical reactions involving the reduced ketyl radical. The presence of organics that are highly reactive with triplet states increases the photosensitized HO_2 radical production of imidazole-2-carboxaldehyde (IC) up to 20 M day^{-1} (Corral-Arroyo et al., 2018). Imidazole-2-carboxyldehyde (IC) is a BrC proxy (absorption spectrum in Fig. S1) and well-known photosensitizer (Corral-Arroyo et al., 2018;González Palacios et al., 2016). Subsequent to the The oxidation of the halide anion by the triplet state of IC leads to, halide radicals ($X^{\bullet}$ and X_2^-), are produced and the ensuing halide radical-radical reactions produce molecular halogen compounds (Reactions 8-11 and 14, Table 1). H_2O_2 is additionally produced by the HO_2 itself reaction of HO_2 and by the reaction between HO_2 and X_2^-. We do not consider further reactivity of H_2O_2 since it is not photolyzed at our the wavelengths used in the present study. The oxidized species X_2, X_2^- and $X^{\bullet}$ are likely recycled into X^- by HO_2 radicals (Reactions 5-9, Table 1). However, a fraction of X_2 may be released into the gas phase (Jammoul et al., 2009), and these recycling processes are determining the effective

efficiency in terms of halogen activated~~ion~~ per photon absorbed by the photosensitizer. ~~De Laurentiis and co-workers suggested that excited triplet states can oxidize bromide faster than OH radicals in sea water (De Laurentiis et al., 2012). Some modelling studies of aerosol chemistry consider halogen chemistry driven entirely by inorganic halogen chemistry~~ (Sherwen et al., 2016b;Sherwen et al., 2016a)~~, while Pechtl et al. claimed that dissolved organic matter may be included as a HOI deactivation pathway~~ (Sarwar et al., 2016;Pechtl et al., 2007)~~. The contribution of photosensitized halogen activation is missing in these models.~~

~~Imidazoles, which include IC, are BrC compounds formed as products from the multi phase chemistry of glyoxal and ammonium sulfate (AS) in aqueous aerosols~~ (Aregahegn et al., 2013;Kampf et al., 2012;Yu et al., 2014)~~. Glyoxal is an important oxygenated volatile organic compound (OVOC) and its dominant known sources on the global scale are biogenic VOC (Stavrakou et al., 2009). Citric acid (CA) serves as a proxy for non-absorbing highly oxidized and functionalized secondary organic compounds in the atmosphere, which are also ubiquitous in marine air (O'Dowd and de Leeuw, 2007). In solution, CA takes up or releases water gradually without phase change over the whole range of relative humidity (RH) values studied here~~ (Lienhard et al., 2012;Zardini et al., 2008)~~.~~

In this work, we quantify the effect of bromide and iodide on the HO_2 production from IC photochemistry and evaluate the iodine activation resulting from the subsequent condensed phase radical reactions by means of Coated Wall Flow Tube (CWFT) experiments. ~~We measured the iodine and HO_2 release from films loaded with IC, CA and bromide or iodide while irradiating with UV light.~~ As a matrix, we use citric acid (CA) that serves as a proxy for non-absorbing highly oxidized and functionalized secondary organic compounds in the atmosphere, which are also ubiquitous in marine air (O'Dowd and de Leeuw, 2007). In solution, CA takes up or releases water gradually without phase change over the whole range of relative humidity (RH) values studied here (Lienhard et al., 2012;Zardini et al., 2008). This allow~~s~~ed us to carefully address the influence of the microphysical conditions on transport and chemical reactions. Finally, we discuss the relevance of our findings for atmospheric sea spray aerosol. ~~Citric acid (CA) serves as a proxy for non-absorbing highly oxidized and functionalized secondary organic compounds in the atmosphere, which are also ubiquitous in marine air (O'Dowd and de Leeuw, 2007). In solution, CA takes up or releases water gradually without phase change over the whole range of relative humidity (RH) values studied here .~~

2 Experimental

2.1 Experimental description

The setup to ~~indirectly detect~~determine HO_2 production in an irradiated laminar coated wall flow tube (CWFT) by scavenging HO_2 with an excess of nitrogen monoxide (NO) has been described in detail in our previous work (González Palacios et al., 2016;Corral-Arroyo et al., 2018) and in the SI (Fig. S2 and S3). Tubes (1.2 cm inner diameter, 50 cm long, Duran glass) coated with mixtures of IC/CA/NaI and IC/CA/NaBr on their inner surfaces were snuggly fit into the temperature and relative humidity controlled CWFT as inserts surrounded by 7 fluorescent lamps (UV-A range, Philips Cleo Effect 20W: 300–420 nm,

41 cm, 2.6 cm o.d., see SI Fig. S1). The flows of N_2 and O_2 were set at 1 L min^{-1} and 0.5 L min^{-1} respectively. The NO concentration (5-10 ml min^{-1} of a mix of N_2 and NO at 100ppm) was always high enough (1 - 2.5 × 10^{13} molecules per cm^3) to efficiently scavenge ~99% of HO_2 produced by the films within 20-50 ms and thus far less than our residence time of 2 s. NO was measured by a chemiluminescence detector (Ecophysics CLD 77 AM). For experiments with bromide, we assumed that the concentration of bromide did not change over the time scale of our experiments and, therefore, the system was in steady-state under irradiation. On the other hand, the concentration of iodide decreased rapidly (within tens of minutes), since the iodine is rapidly released into the gas phase. Therefore, ~~, so~~ we ~~assessed~~ determined the NO loss from the first few minutes of irradiation for reporting HO_2 production rates for experiments using iodide in films.

Iodine release into the gas phase was observed by converting all gas phase iodine compounds to I_2O_5 following a procedure developed by Saunders et al. (Saunders and Plane, 2006). Part of the flow from the reactor (0.1 L min^{-1} out of 1.5 L min^{-1}) was mixed with 0.2 L min^{-1} of O_2/O_3 (1%), and this mixture was fed into a quartz reactor with 0.07 s residence time, which ~~is~~ was irradiated with a Hg penray lamp (184 nm). The O_2/O_3 (1%) mixture was produced by a discharge in pure O_2 and quantified with a photometric ozone analyzer. In the quartz reactor, a~~A~~ll iodine compounds ~~are~~ were readily photolyzed and oxidized to I_2O_5, which polymerized and produced particles via homogeneous nucleation (Carpenter et al., 2013;Saunders and Plane, 2006). The resulting aerosol flow was led to a Scanning Mobility Particle ~~Analyzer~~ Sizer (SMPS) through aerosol tubing with a residence time of around 20 seconds. T~~t~~he SMPS consisted~~ing~~ of a home-made differential mobility analyzer (DMA, 93.5 cm long, 0.937 cm inner diameter, 1.961 outer diameter~~,~~) and a Condensation Particle Counter (CPC, Model 3775, TSI Inc.). ~~and~~ T~~t~~he mass of the I_2O_5 particles was determined from ~~measuring~~ their size distribution ~~with the SMPS consisting of a home-made differential mobility analyzer (DMA, 93.5 cm long, 0.937 cm inner diameter 1.961 outer diam.) and a Condensation Particle Counter (CPC, Model 3775). The I_2O_5 particle~~with the density ~~was~~ assumed to be 2.3±0.3 g cm^{-3} following Saunders et al. (Saunders and Plane, 2006). The particle mass was converted to an equivalent I_2 release assuming the stoichiometry of I_2O_5. We were able to measure particles reliably only ≥20 nm in diameter (Fig. S4, SI). This method does not distinguish between iodine and any other volatile iodine compound, which ~~can~~ may be oxidized ~~up~~ to I_2O_5 as well. HOI or IO might be produced in the films by oxidation of halide radicals or molecular halogens, but they are likely not significant products i~~,~~n absence of O_3 in the CWFT. Hence, we~~We~~ rely on our proposed mechanism (~~Figure~~ Fig. 1) and assume that iodine activation is dominated by production of I_2.

Aqueous solutions containing halides (10^{-8} M, 10^{-5} M and 0.01 M for iodide and 10^{-5} M and 0.01 M for bromide) were prepared beforehand. For each experiment, 76.6 mg of CA and 4 mg of IC (2.5 mg of IC for the experiments measuring iodine release) were dissolved in different volumes of a halide solution in order to get different halide concentrations in the films. Once prepared, a solution was deposited in the glass tube while rolling and turning the tube in all directions at room temperature under a gentle flow of N_2 humidified t~~N~~$_2$ ~~t~~o the RH later used in experiments. This procedure was necessary to ensure homogeneous thin films checked by visual inspection and to prevent~~ed~~ the film from drying out ~~during~~ prior to the experiments. Freshly prepared solutions were always used to prepare the films. After final equilibration in the CWFT, c~~C~~oncentrations in the film were 6 M for CA, 0.7 M for IC, between 10^{-8} M and 0.01 M for iodide and between 10^{-4} and 0.01 M for bromide (0.4

M of IC and 33mM of iodide for iodine release measurements) at around 35% RH at 20°C. These were calculated assuming that the water content in the film was controlled by the hygroscopicity of CA only, as parameterized by Zardini et al. (Zardini et al., 2008). Films are expected to be liquid at 35 % RH and have a viscosity of around 10 - 100 Pa s (Song et al., 2016). For iodide, just two measurements were made for each film, since iodide is consumed rapidly, while for bromide we made 4-6 consecutive measurements were made for each film. One measurement is made by theconsisted of comparingson of the signals of NO before and after switching on or off the UV lamps. For the CWFT experiments, where in which we measured the release of I_2 was measured, films were loaded with 2.5 mg of IC, 76.6 mg of CA (6.5% in molar ratio) and 313 µg of NaI, corresponding to concentrations of 0.4 M, 6 M and 33 mM of IC, CA and iodide respectively, and the iodine release into the gas phase at 34% RH was followed uninterruptedly.

2.2 Chemicals

The chemicals used were imidazole-2-carboxaldehyde (>99%, Aldrich), citric acid (Fluka), sodium bromide (Sigma-Aldrich) and sodium iodide (Sigma-Aldrich).

3 Results

3.1 HO_2 production, scavenging and release

Figure 2 2 presents the HO_2 radical release in the CWFT as a function of halide concentration from films loaded with IC/CA/NaBr and IC/CA/NaI. Error bars are the standard deviation of several multiple measurements in the same film. The HO_2 radical release exhibits first an increase starting from the baseline in absence of halides reaching a peak at about 8 ×x 10^{11} cm^{-2} min^{-1}. and later a decrease below that for higher halide concentrations. For comparisonThe baseline HO_2 release is, due to HO_2 production for the IC/CA system without any halides is shownfrom the reaction of the ketyl radical $PH^{\bullet}$ with O_2 as the (blue solid line in Fig. 31), with $PH^{\bullet}$ being produced from the oxidation of CA by the triplet P*(t). ,-Theis baseline was (measured here again)in this study and is consistent with our previous studies value (Corral-Arroyo et al., 2018;González Palacios et al., 2016). The photosensitized oxidation of CA resulting in the production of the ketyl radical ($PH^{\bullet}$, see Figure 1), followed by reaction of $PH^{\bullet}$ with O_2 to lead to the formation of HO_2 (upper red arrow in Figure 1), in absence of halide ions, has been discussed in detail in those studies. Increasing the halide content beyond the peak concentration observed in Fig. 2 resulted in a decrease of HO_2 below the baseline.

Once the halide concentration is increased, HO_2 production increases. We expectClearly, Figure 2 shows that even aOur results can be explained by small amount of halides can start to contributinges to the reduction of P* due to their their ability of halides to donate an electron more efficiently than CA. This wouldshould have ledleads to an increased production of $PH^{\bullet}$ and thus increased production of HO_2 (Figure Fig. 1). The observed HO_2 production and release is enhanced above the baseline from at 1.2 ×x 10^{-7} M oforf iodide and 5 ×x 10^{-4} M for bromide.,- which This implies that the rate coefficient for the reduction of the IC triplet (P*) by iodide is also 3 orders of magnitude faster than that for reduction by bromide, in line with the rate

coefficients for ~~reaction 5~~R5 in Table 1 measured by~~.~~ Tinel et al. (Tinel et al., 2014) ~~measured the rate coefficients between the triplet state of IC and bromide and iodide (reaction 5)~~ as 5.33×10^9 M^{-1} s^{-1} and 6.27×10^6 M^{-1} s^{-1}, respectively. ~~The difference is roughly three orders of magnitude in line with our observations.~~

After the oxidation of the halide ion by the triplet state, it is expected that a cascade of fast reactions take~~s~~ place leading to the production of X_2^- and molecular halogens (X_2). Most of these halogen species~~, including the molecular halogen,~~ react rapidly with HO_2 (reactions 5-9 in Table 1), which ~~leading to~~explains the drop of the HO_2 release at high halide concentrations ~~of~~. Additionally, HO_2 radicals also ~~react with each other~~undergo self-reaction meaning that this scavenging pathway will be more relevant at high concentrations of halides, where more HO_2 is produced (8×10^5 M^{-1} s^{-1}) (Bielski et al., 1985).

The reaction of HO_2 with X_2^-, the main HO_2 scavenging reaction~~s~~ (~~R12-R16~~R14) ~~shown in~~ (Table 1) ~~are~~ is ~~typically~~ faster for the ~~iodide~~ iodine species than for the ~~bromide~~ bromine species, which induces a suppression of the HO_2 release at lower concentrations for iodide than for bromide. In this way, the majority of HO_2 is ~~mostly~~ scavenged before being released into the gas phase for films with concentrations of iodide above 10^{-3} M and of bromide of 10^{-2} M. The ratio of the rate coefficients of the triplet with iodide and bromide (R5) is higher than the ratio of the rate coefficients of HO_2 with ~~iodide~~ iodine and ~~bromide~~ bromine species, which induce the recycling (R12-16). We suspect that this is the reason why the HO_2 release drops faster with concentration for bromide than for iodide.

In our recent work (Corral-Arroyo et al., 2018), a~~A~~ steady-state kinetic model was developed ~~about~~ treating IC photochemistry ~~assuming steady state in our recent work~~ (Corral-Arroyo et al., 2018)~~, where we estimated the~~and HO_2 release from films of IC/CA as a function of concentration of IC, relative humidity, film thickness or additional organic triplet scavengers. Here, we ~~We~~ extended ~~the~~ that model ~~by Corral-Arroyo, 2018~~ to include the scavenging of the triplet state of IC by halides ~~(~~Tinel et al., 2014) ~~(reaction 4) (instead of an additional organic donor)~~. The inter-halogen conversion reactions (reactions 8-11) and a set of HO_2 scavenging reactions 12 – 16 (Table 1) were added. We also added the photolysis of iodine by integrating the product of the irradiance spectrum of the lamps used (Fig. S1) and the absorption spectrum of iodine (Choi et al., 2012). Due to the fast equilibrium between ~~We treated~~ I_2 and I_3^-~~-~~, their concentration ratio remained fixed by the equilibrium constant (Table 1), meaning effectively that both have the same sources and sinks~~as the same species~~. Further details of the reactions and rate coefficients are given in the SI. Using the literature values for each reaction, t~~T~~he model capture~~d~~s the general trend of HO_2 release with a maximum and a downward slope ~~down~~ upon increasing concentrations of halides ~~with a shift towards higher concentrations.~~ However, ~~Our~~the model ~~was overpredict~~over predicte~~d~~ding the HO_2 ~~radical~~ release at middle and high concentrations of halides (10^{-5} – 10^{-1} M). Therefore, in the process of optimization to adjust the model output to observations, the inter-halogen conversion reactions (reactions 8-11) were kept at their literature values, while the HO_2 scavenging reactions 12 – 16 were ~~tuned~~decreased ~~downwards,~~ as described in the SI. ~~to obtain reasonable model results we reduced the values of the rate coefficients for reactions R11-15 keeping them equaled to each other (SI).~~ Such ~~tuning is~~adjustments were justified because~~The model results allow us to assess the HO_2 release (Figure 2), and the efficiency in the cycling of the radicals, which~~

will be explained further below. We found that the HO_2 release was underpredicted at middle and high concentrations of halides. We decided to keep the inter-halogen conversion reactions (reactions 8-11) at their literature values and tune the HO_2 scavenging reactions 12 – 16. To obtain reasonable model results, they were reduced as explained in the SI. The model captures the general trend with a maximum and a slope down upon increasing concentrations of halides with a shift towards higher concentrations. The model results allow us to assess the HO_2 release (Figure 2), and the efficiency in the cycling of the radicals, which will be explained further below. Differences between model and experimental results might come literature rate coefficients measured in dilute aqueous solution may not necessarily be the same at from by thea high solute strength, of the solution of the present study and prevalent in atmospheric aerosol which was the case for our filmsfeaturing different rate coefficients of for the scavenging of triplet states by halides and of the HO_2 scavenging reactions in than in dilute aqueous solutions (where the used literature rate coefficients were measured) versus those in the high solute strength solution of the present study and prevalent in atmospheric aerosol. We decided to keep the inter-halogen conversion reactions (reactions 8-11) at their literature values and tune the HO_2 scavenging reactions 12 – 16. To obtain reasonable model results, they were reduced as explained in the SI. There is evidence that hydrogen bonded transition states are involved in electron transfer (IvkovicJensen and Kostic, 1997), proton coupled electron transfer, hydrogen abstraction reactions (Mitroka et al., 2010) and quenching reactions between triplets and salts (Kunze et al., 1997). Reduced activity of reactants and water may thus act to reduce reaction rates. However, However, wewe refrained from adding more and ill-constrained processes and parameters to achieve better apparent fit. As shown in Figure. 2, after optimization, the maximum HO_2 release rates are well reproduced considering the scatter in the data. The position of the maximum is determined by the ratio between the scavenging of triplet states by halides and the HO_2 scavenging reactions. The predicted maxima are shifted towards higher halide concentrations compared to our observations. This can be explained , if CA derived radicals reacted with halogen radicals to produce halogen-containing organic compounds, as already observed in aquatic media (Roveretto et al., 2019), which could result in a partial scavenging of halogens. Another feature captured by our model is thbut the downward slopes of observed HO_2 production being greater for films containing bromide than those with iodide. are consistent with the observation for both iodide and bromide. The position of the maximum is determined by the ratio between the scavenging of triplet states by halides and the HO_2 scavenging reactions. An additional process may be that Since we kept the rate coefficient of the scavenging of the triplets fixed, the tunable parameters were the HO_2 scavenging reactions. Our model was overpredicting the HO_2 radical release at middle and high concentrations of halides (10^{-5} – 10^{-1} M). Therefore, to obtain reasonable model results we reduced the values of the rate coefficients for reactions R11-15 keeping them equaled to each other (SI). CA derived radicals can could react with halideshalogen radicals and produce halogen-containing organic compounds, as already observed in aquatic media (Roveretto et al., 2019). This can could result in a partial scavenging of the halides radicalshalogens and it might be an explanation for the need to decrease the reaction In spite of the differences, the model correctly predicts the stronger slope of the decrease of HO_2 release with halide concentration for the case of bromide in comparison to that for iodide remaining differences.

3.2 Iodine activation

~~We performed CWFT experiments in which the iodine release was measured as described in the experimental section. The HO_2 release was measured separately with a separate film under the same conditions and within the same range of time.~~

Figure 3 shows ~~that~~ the release of iodine and the corresponding HO_2 release from a single film continually irradiated for 140 ~~hours~~min. Iodine release ~~–~~strongly increased ~~immediately~~ with irradiation, ~~and~~peak~~ings~~ after ~~ten~~ only several minutes of irradiation and ~~falls~~falling off over the following 60 minutes. The maximum ~~in~~ of the iodine release was ~~observed after several minutes of irradiation being about~~ 5.5×10^{13} molecules min^{-1} cm^{-2}. When normalized to the initial amount of iodide present in the film, this corresponds to a iodide life-time of around 8400 s, thus a bit more than 2 hours. ~~W~~The steady-state ~~iodine release~~ model prediction is 4.9×10^{15}~~3~~ molecules min^{-1} cm^{-2} at the initial concentration of iodide, which cannot be directly compared to the measurement, because the measurement with the SMPS could not resolve a sharp initial release. Note in addition that the model is not following the system over time. ~~Figure 3 also presents t~~The corresponding HO_2 release versus time ~~, which~~ was measured ~~separately~~ with a separate film under the same conditions and within the same range of time. Initially, HO_2 is entirely depleted as expected for the high iodide concentration of 33 mM used (see ~~Figure~~ Fig. 2). Then, HO_2 release increases linearly until 90 minutes ~~before it reaches~~when a steady state is obtained at 3×10^{11} molecules min^{-1} cm^{-2}, which is the same as that measured in absence of iodide (Corral-Arroyo et al., 2018) (blue arrow in ~~Figure~~ Fig. 3, blue line in Fig~~ure~~. 2). When comparing to Fig.~~ure~~ 2, the evolution of the HO_2 release with time indicates that ~~most likely~~ a drop in the iodide concentration from 33 mM to below 10^{-4} M ~~occured~~occurred. ~~The maximum in the iodine release was observed after several minutes of irradiation being about 5.5×10^{13} molecules min^{-1} cm^{-2}. The iodine release model prediction is 4.9×10^{13} molecules min^{-1} cm^{-2} at the initial concentration of iodide. In view of the uncertainty of many of the parameters used in the model, the consistency between model and observation is rather surprising. Photolysis and scavenging rate coefficients can be different in aqueous solutions (where the used rate coefficients were measured) and in organic matrix (Lignell et al., 2014;Mitroka et al., 2010;IvkovicJensen and Kostic, 1997;Kunze et al., 1997), and also the simple steady state assumption is bearing uncertainties. It seems that iodine release is a more robust observable than HO_2 radicals, and the model apparently captures the halogen chemistry reasonably well.~~ The total integrated I_2O_5 mass measured over the whole observation period corresponds to 70(±10) % of the iodide added to the film. As indicated in the SI, we could not measure the mass from particles smaller than 20 nm of diameter, so the mass calculated is a lower limit of the real mass released from the film~~s~~. ~~The~~ Together with the synchronized behavior of both releases (HO_2 and I_2), this indicates that iodide is ~~significantly consumed~~nearly completely depleted in our films after 100 minutes of irradiation and presumably most of iodide is converted into molecular iodine, consistent with the life-time estimate based on the observed maximum release rate. ~~As indicated in the SI, we could not measure the mass from particles smaller than 20 nm of diameter, so the mass calculated is a lower limit of the real mass released from films.~~ Alternatively, sinks of halides in the films could be the reaction of halide radicals ($I^{\bullet}$ or I_2^{-}) and of HOI or HOBr with organics producing Org-X (Abrahamsson et al., 2018;Gilbert et al., 1988;Roveretto et al., 2019) or further oxidation of iodine to iodate, which was beyond the scope of our study.

The efficiency of the iodine activation depends on the different competing processes occurring in the P catalytic cycle and the ones involving halogen radical chemistry (~~Figure~~ Fig. 1). Oxygen, CA and halides compete for the triplet. Once the triplet oxidizes the halide, the radicals produced can be recycled back to halide ~~(recycling A)~~ or produce the molecular X_2 compounds bromine and iodine. X_2 ~~These~~ can be recycled back to X_2^- (recycling B) or escape to the gas phase. In spite of the inability of the steady-state model to follow the iodide depletion over time, we can use the model to assess these recycling pathways. For iodine, the model predicts that around 50% of halogen atoms produced are released to the gas phase as molecular halogen (40% RH, $D_{HO2} = 3.5 \times 10^{-12}$ cm^2 s^{-1} and $D_{I2} = 2 \times 10^{12}$ cm^2 s^{-1}) indicating that the fate of around half of iodide radicals is ~~the~~ recycling and the other half is leaving the condensed phase as iodine. ~~This is the overall result of several competing chemical processes.~~We argue that HO_2, $X^\bullet$ and X^- compete for X_2^-, and when X_2 is finally produced, it can diffuse out or react with HO_2 to produce X_2^-. ~~Our model predicts that the ~ 50 % of the I radicals ($I^\bullet$ and I_2^-) produced are recycled back to iodide (around 40% for bromide),~~ According to our model, halogen atom recycling ~~and these numbers do~~ does not change significantly with RH, however, this is not the case for molecular halogens. ~~In turn, bBased on the model, t~~The predicted efficiency in the release of molecular iodine ~~or bromine is~~was ~~then~~ about 85 – 95 % at RH = 40% ~~and > 99 %, respectively (5 – 15 % and < 1 % recycling back to X_2^-, respectively),~~ and ~~which~~ decreased to 45 – 65 % ~~and 97.5 %, respectively (15 – 50 % and 2,5 % recycling back to X_2^-, respectively),~~. ~~u~~Upon~~when~~ the diffusion coefficient was ~~decreasing~~ decreased ~~the diffusion coefficient~~ by one order of magnitude~~, the efficiency in the release of molecular iodine or bromine is then about 45 – 65 % and 97.5 % respectively (15 – 50 % and 2,5 % recycling back to X_2^-, respectively)~~. For molecular bromine, the efficiency of ~99% dropped by 2.5% when D_{Br2} was decreased by the same amount. ~~On the other hand, upon i~~Increasing the diffusion coefficient by one order~~s~~ of magnitude increased the efficiency in the release of molecular iodine or bromine ~~is then about~~to 97 − 99.5 % ~~for iodine~~ and almost 100%~~,~~ respectively~~for bromine~~. Thus, ~~relative humidity, via~~changing diffusivity due to change RH~~,~~ may have ~~has~~ a strong impact on the cycling and thus the fate of X_2 ~~(release or recycling)~~, but not ~~that much on the cycling of the~~for X radicals.

4 Conclusions and atmospheric implications

We investigated the influence of halides on the photochemistry of imidazole-2-carboxaldehyde and its oxidative capacity. The addition of both iodide and bromide increased the HO_2 radical production in the system IC/CA. This can be explained by the oxidation of halide ions by IC triplet being several orders of magnitude faster than the corresponding oxidation of CA (when $[I^-] > 10^{-6}$ M then $k_I\text{-}[I^-] > k_{CA}[CA]$) (Tinel et al., 2014;Corral-Arroyo et al., 2018). The halogen radical species resulting from the reaction with the triplet scavenge away the HO_2 produced preventing it to leave the film and thus maintaining the capacity to participate in red-ox cycles with the halide species.

Typical concentrations of iodide and bromide in sea spray particles ~~is~~ are 10^{-6} M (Baker, 2004, 2005;Pechtl et al., 2007) and 8×10^{-3} M (Herrmann et al., 2003), respectively. At the sea surface many kinds of chromophoric organic compounds are present, including biomolecules, carbonylic and carboxylic compounds (CDOM) (Chen et al., 2016;Quinn et al., 2015), which are

uplifted together with sea spray particles (Hunter and Liss, 1977;Cincinelli et al., 2001). Based on our results, halides are concentrated enough in atmospheric aerosol particles to contribute to the radical production. Assessment of chlorine activation via IC as chromophore and sensitizer reacting with chloride, which is present in higher concentrations in sea salt aerosol particles (~5.4 M) (Herrmann et al., 2003), was beyond the scope of this study. While the ratio of chloride to bromide or iodide is higher than the inverse ratio of the corresponding rate coefficients (Tinel et al., 2014), the complex radical chemistry and kinetics require detailed attention to understand impacts on chlorine activation and photosensitized HO_2 production. ~~As we demonstrated, it~~Halogen activation ~~may~~ depends on the kinetics of the triplet states with halide ions and of the recycling reaction that control the halogen and HO_2 yields, so that different relative yields of the two may be expected for different photosensitizing BrC or CDOM species. Furthermore, interactions among the halogens, i.e., bromine with iodine, or either of them with chlorine, have not yet been considered here~~coupled~~~~the properties of the triplet states to what degree the coupling with bromide and iodide reactions and leads to halogen activation and to what degree HO_2 production is affected~~. An additional aspect is that p~~P~~rimary organics present in nascent sea spray particles or on the ocean surface may themselves scavenge triplet states with ~~faster~~ rates on the same order of magnitude as iodide ~~than CA (used as a proxy for secondary organics) and in the same order of magnitude as iodide~~ (Canonica, 2000), thus diminishing the capacity for halogen activation~~ initially~~. ~~Though~~Although, we suspect that the complex secondary radicals, e.g., alkoxy radicals, would still propagate the triplet induced capacity to oxidize halides. ~~These results can be partially extended to chloride, which is present in higher concentrations in sea salt aerosol particles (~5.4 M) (Herrmann et al., 2003) also being less reactive than bromide and iodide~~ (Tinel et al., 2014)~~. Further studies must be done for chloride to better understand chlorine activation and HO_2 photosensitized production.~~

~~We~~ In the introduction section we estimated the maximum extent of iodine activation in a solution containing 10^{-6} M based on a steady-state triplet concentration of 10^{-10} M to ~~previously calculated the iodine activation rate of~~ be 2.5×10^{-7} M s^{-1}, corresponding to a rather short lifetime of iodide of a few seconds only. Based on the results obtained, we can refine this number. We note that the experiment in Fig~~ure~~. 3 cannot be directly extrapolated to atmospheric conditions due to the high 33 mM iodide concentration used, which suppresses the triplet concentration to 10^{-12} M. In addition, the viscous films were 3.4 µm thick, thus beyond atmospheric particle size ranges. We therefore run model calculations with 10^{-6} M iodide, a film thickness of 0.5 µm and with the IC concentration adjusted such that the triplet concentration at steady state reached 10^{-10} M. Under these conditions, the iodine release is estimated at 4.1×10^{-7} M s^{-1} at 35% RH and roughly a factor of 2 larger when the diffusion coefficients are set to the 10^{-6} cm^2 s^{-1} range for a low viscosity liquid. ~~calculated the iodine produced internally by reaction between triplets and iodide to illustrate the importance of this iodine activation pathway in comparison to the one triggered by the oxidation of iodine iodide by ozone (O_3). Assuming a concentration of 10^{-10} M for triplet states and 10^{-6} M for iodide in sea spray particles and a second order rate coefficient of 5×10^{-7} M^{-1} s^{-1}~~ (Tinel et al., 2014)~~, the first order iodine activation by photosensitized chemistry may get to 5×10^{-7} M s^{-1}. To compare this number with the~~and now Next, we compare ~~to the~~se rates to the ~~calculated~~estimated oxidation rate by O_3~~, detailed in the supporting information. In~~first, in a reacto-

diffusion limited regime., ozone uptake and reaction with iodide can lead to 1.1 × 10^{-7} M s^{-1}. To accomplish this, we calculate First,the uptake coefficient, γ, of O_3 under the assumption that the reaction proceeds in the reacto-diffusive kinetic regime, thus for a viscous particle with low diffusivity is:

$$\gamma = \frac{4H_{O_3}RT}{\omega_{O_3}}\sqrt{D_X k_b^{II}[I]_b} \quad (1)$$

where R is the universal gas constant and At 25°C, the mean thermal velocity of ozone, ω_{O3}, is 318 m s^{-1} at T=25°C. Assuming We calculate that γ = 2.7 × 10^{-8} using ozone a Henry's law constant, (H_{O3}), of 0.14 M atm^{-1} (Berkemeier et al., 2016), a diffusion coefficient of ozone, (D_{O3}), of 1 × 10^{-12} cm^2 s^{-1} in a viscous organic particle (Berkemeier et al., 2016), which corresponds to an aqueous CA particle at ~ 40% RH at room temperature or to a CA particle at ~70% RH at -20°C (Lienhard et al., 2014), a bulk reaction rate coefficient, and $k_{O3}k_b^{II}/4$ –, (O_3 + I^-) asof 4.2 × 10^9 M^{-1} s^{-1} (Magi et al., 1997), and the same particle phase iodide concentration, $[I]_b$, of -10^{-6} M, as above., γ the ozone uptake coefficient would be 2.7 × 10^{-8} (eq.1) under the assumption that the reaction proceeds in the reacto-diffusive regime. For the purpose of this back of the envelope calculation, we neglect pParticle size effects.

Where H_{O_3} is the Henry's law constant, R is the gas constant, T is temperature, ω_{O_3} is the mean thermal velocity of ozone, D_x is the diffusion coefficient, k_b^{II} is the rate coefficient of the reaction between ozone and iodide ($k_{O3/4}$ as 4.2 × 10^9 M^{-1} s^{-1}) and $[I]_b$ is the concentration of iodide in aerosol particles. Note or contributions from a surface reaction that equation (1) does not fully capture all details of the reaction kinetics, as on one hand the kinetics may switch from this reaction diffusion limited regime to a bulk reaction limited regime, depending on particle size, diffusivity of O_3 and iodide concentration. In addition, the contribution of a surface reaction remains open (see Moreno et al. (Moreno et al., 2018) were neglected for this simple comparison.for an in depth analysis of this kinetics). Based on γ

, U, tThe rate of O_3 uptake, U ,(in molecules s^{-1} per particle) and thus of iodide oxidation (as an upper limit to iodine activation), can be calculated via:by

$$U = \pi C_{g,O_3}\omega_{O_3}r^2\gamma\,, \quad (2)$$

Wwhere C_{g,O_3} is the concentration of ozone in the gas phase in molecule cm^{-3} and r is the radius of the particle.

For a gas-phase concentration mixing ratio of 100 ppb (2.5 × 10^{12} molecule cm^{-3}) and a particle 500 nm in diameter, *the uptake of ozone (U) (eq. 2) and potential iodine activation will* be normalization to the particle volume yields an iodide turnover of 1.15.5 × 10^{-87} M s^{-1}, which is an order of magnitude below that estimated for the photosensitized oxidation under comparable conditions.

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On theOn the other hand, we can consider a more dilute aqueous particle or one that is dominated by inorganic ions only, where the liquid phase diffusion coefficient is high and when assuming that ozone is fully equilibrated with the aqueous phase

~~of the particle (assuming~~the solubility of O_3 is lower, H_{O_3} = 0.012~~14~~ M atm^{-1} as in pure water (Sander, 2015). O_3 remains well-mixed throughout the particle due to the low iodide content. For the same iodide content and O_3~~), thus at high RH, where diffusive mixing of the aqueous phase is fast, at atmospheric concentrations~~ mixing ratio as above~~(100ppb)~~ the iodine activation ~~will be~~would become 5.0~~.9~~ × 10^{-6}~~5~~ M s^{-1}~~.~~, thus about a factor of 5 higher than the estimate for the photosensitized oxidation under conditions with high RH and high diffusivity. We note that

~~A~~at 0~~.~~° zenith angle, ~~the ratio of the excitation rates of IC from t~~the ~~sun~~ solar actinic flux is ~~spectrum and that used in our experiments~~about 3 times greater than~~t~~ the UV lamps we used in the experiment, and thus excitation rates of IC may be 3 times faster than what was used here. ~~(j_{sun}/j_{lamps}) is about 2.83. Therefore, in terms of irradiation our results can be extrapolated confidently to the atmosphere.~~ We conclude that photosensitized iodine production is relevant for aerosol sea spray aerosol particles containing chromophores under ~~dry~~ lower RH conditions or lower temperature when the reactive uptake of ozone is slow. Under humid conditions and with less organics present the activation via reaction with ozone ~~will~~ may dominate, though still with a significant contribution from photosensitized chemistry~~likely be more relevant~~.

~~-~~We noted the existence of a cycling in halide radical chemistry that shuts down the HO_x chemistry and, simultaneously, prevent the release of molecular halogens to the gas phase. Also t~~T~~his cycling strongly depends on the diffusion properties of the matrix, reaching a greater cycling efficiency when diffusion is low and lower efficiency when diffusion is fast. Even so, the release is not ~~deeply~~ entirely reduced under a wide range of diffusion regimes and a large fraction of the iodine produced (50%-100%) will be released. Based on the model predictions, we suspect that ~~the~~ bromine activation behaves in a similar way ~~in presence of bromide~~as iodine activation, since the impacts on HO_2 release were ~~comparable to those for the iodide case~~similar ~~processes are occurring for bromide, which opens up new fields of research~~.

Code and data availability. The data underlying Fig~~ures.~~ 2 and 3 and the matlab codes of the steady-state model calculations are available as supporting files. ~~for simulations performed under Sect. 3.1 and 3.2 are available in…~~

Author contributions. The scientific contributions were provided by all coauthors.

Competing interests. The authors declare that they have no conflict of interest.

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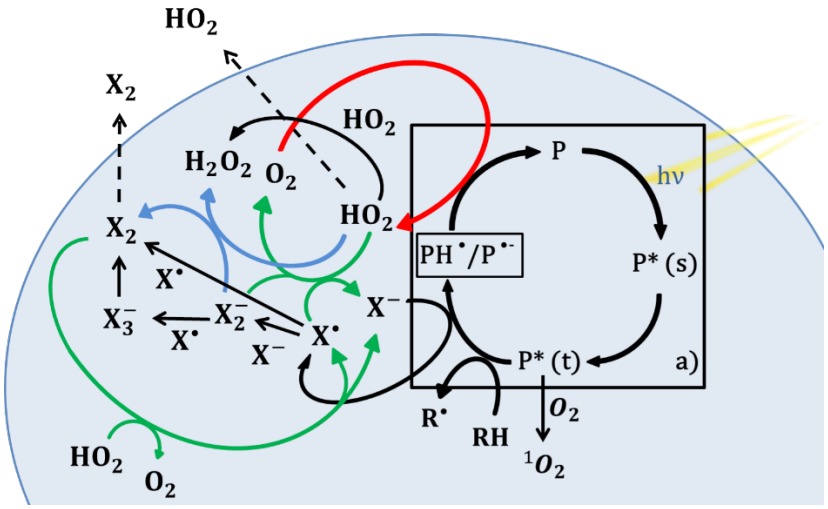

Figure 1. Photochemical catalytic cycle of IC (box a) and halide radical chemistry induced in a particle. IC is a photosensitizer (P) that first absorbs light, excites to its singlet state P*(s), and transitions to its triplet state P*(t), which reacts ~~leading to the triplet state,~~ which reacts with an H atom/electron donor (~~DH~~ RH and X^-) to produce the reduced ketyl radical ($PH^•$) and halide radicals ($X^•$). The halide radicals can produce molecular halogen (X_2) or X_2^- by reacting with X^-. $PH^•$ may transfer an H atom or electron to an acceptor, such as O_2 producing HO_2 radicals. HO_2 can recycle the halide radicals previously produced into halides or oxidize further the X_2^- to produce halogen molecules. HO_2 radicals can be released into the gas phase or react within the particle with halide radicals or with itself. Solid lines refer to reactions and dashed lines refer to transfer from the condensed to the gas phase. The r~~R~~ed ~~reaction~~ arrow~~s~~ indicate~~s~~ ~~reactions promoting~~ HO_2 production, green arrows indicate ~~reactions of~~ recycling of halides promoted by HO_2 and blue arrows indicate the reaction~~s~~ of X_2^- ~~promoted by~~with HO_2 to form X_2^-~~.~~. Rate coefficients are provided in Table 1.

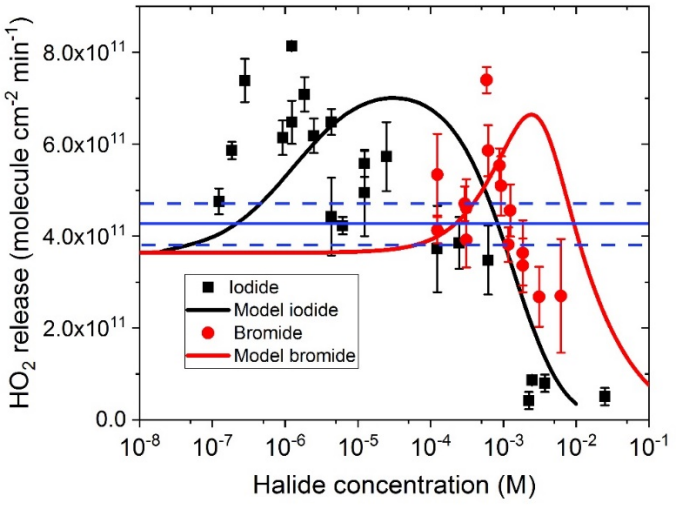

Figure 2. HO_2 release at 34% RH from films with 4 mg of IC, 76.8 mg of CA and various concentrations of bromide (red circles) and iodide (black squares). Error bars indicate the standard deviation of ~~between 2-6~~ measurements in the same film. The blue line and dashed blue lines indicate measured HO_2 production and uncertainty, respectively, from films with the same IC and CA concentration but in absence of halides. Solid black and red lines are fits using the model described in the text below.

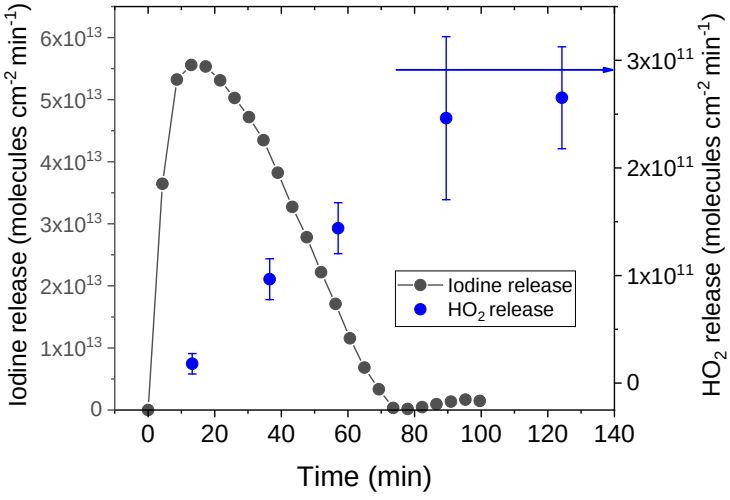

Figure 3. Iodine release ~~(black), measured as~~calculated from the measured mass size distribution of iodine oxide particles produced by oxidation of iodine species released from the CWFT. The left y-axis is expressed as equivalent I_2 release (~~left y-axis~~grey circles), and the right axis is the corresponding HO_2 release (blue~~, right y-axis~~ circles) into the gas phase versus time while irradiating a film in the CWFT loaded with 2.5 mg of IC, 76.8 mg of CA and 313 µg of NaI and equilibrated at 34% RH (33 mM I^-). The blue arrow indicates the HO_2 release expected for the film in absence of iodide.

Table 1. Chemical reactions and the corresponding literature rate coefficients of halide and HO_2 radical chemistry

No	Reaction	Rate coefficient (X=Br) $M^{-1} s^{-1}$	Rate coefficient (X=I) $M^{-1} s^{-1}$	Reference
R1	$IC \rightarrow IC^{3*}$	$1 \cdot 10^{-3}$*	$1 \cdot 10^{-3}$*	Corral-Arroyo
R2	$IC^{3*} + O_2 \rightarrow IC + {}^1O_2$	$3 \cdot 10^{9}$	$2.6 \cdot 10^{9}$	Canonica
R3	$IC^{3*} \rightarrow IC$	$6.5 \cdot 10^{5}$*	$6.5 \cdot 10^{5}$*	Corral-Arroyo
R4	$IC^{3*} + CA \rightarrow ICH^{\bullet} + CA^{\bullet}$	90	90	Corral-Arroyo
R5	$IC^{3*} + X^{-} \rightarrow IC^{\bullet -} + X^{\bullet}$	$6.27 \cdot 10^{6}$	$5.33 \cdot 10^{9}$	Tinel
R6	$ICH^{\bullet} + O_2 \rightarrow IC + HO_2^{\bullet}$	$1 \cdot 10^{9}$	$1\text{-}5 \cdot 10^{9}$	Maillard
R7	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2$	$8 \cdot 10^{5}$	$8.3 \cdot 10^{5}$	Bielski
R8	$X^{-} + X^{\bullet} \rightarrow X_2^{-\bullet}$	$9 \cdot 10^{9}$	$1.1 \cdot 10^{10}$	Nagarajan/Ishigure
R9	$X_2^{-} + X^{\bullet} \rightarrow X_3^{-}$	-	$8.4 \cdot 10^{9}$	Ishigure
R10	$X^{\bullet} + X^{\bullet} \rightarrow X_2$	-	$1.9 \cdot 10^{10}$	Ishigure
R11	$X_2 + X^{-} \leftrightarrow X_3^{-}$	$2.7 \cdot 10^{4}$ [E]	768[E]	Bianchini/Morrison
R12	$HO_2^{\bullet} + X^{\bullet} \rightarrow O_2 + HX$	$1.6 \cdot 10^{8}$	-	Wagner
R13	$HO_2^{\bullet} + X_2^{-\bullet} \rightarrow O_2 + HX + X^{-}$	$1 \cdot 10^{8}$	-	Wagner
R14	$HO_2^{\bullet} + X_2^{-\bullet} \rightarrow HO_2^{-} + X_2$	$9.1 \cdot 10^{7}$	$4 \cdot 10^{9}$	Wagner/Ishigure
R15	$HO_2^{\bullet} + X_2 \rightarrow O_2 + X_2^{-\bullet}$	$1.5 \cdot 10^{8}$	$1.8 \cdot 10^{7}$	Bielski/Schwarz
R16	$HO_2^{\bullet} + X_3^{-} \rightarrow X^{-} + H^{+} + O_2 + X_2^{-\bullet}$	$<1 \cdot 10^{7}$	-	Bielski
R17	$X_2 \xrightarrow{h\nu} 2\,X^{\bullet}$	-	0.01*	-/Choi

Source of rate coefficients: (Ishigure et al., 1988;Nagarajan and Fessenden, 1985;Schwarz and Bielski, 1986;Bianchini and Chiappe, 1992;Bielski et al., 1985;Morrison et al., 1971;Wagner and Strehlow, 1987;Tinel et al., 2014;Maillard et al., 1983;Canonica, 2000;Corral-Arroyo et al., 2018;Choi et al., 2012) *First order rate coefficient (s^{-1}). [E]Equilibrium constant (M^{-1}).