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Iodide conversion to iodate in aqueous and solid aerosols exposed to ozone

Carolina Moreno, María-Teresa Baeza-Romero,* Mikel Sanz, Óscar Gálvez, Vicente López Arza, James C. Ianni and Eva-María Espildora-García

The aqueous-phase and surface reactions of ozone (O₃) with iodide (I⁻) in/on seawater have been recently been found to be a strong atmospheric source of iodine.

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Iodide conversion to iodate in aqueous and solid aerosols exposed to ozone†

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The aqueous-phase and surface reactions of ozone (O₃) with iodide (I[−]) in/on seawater have been recently been found to be a strong atmospheric source of iodine. In addition, ozone also reacts with I[−] in solid and aqueous sea-salt aerosol. However, the primary products of the heterogeneous reactions of ozone with I[−] have not been clarified. In this paper, solid and aqueous KI aerosols have been exposed to ozone in an aerosol flow tube system and I[−] and iodate (IO₃[−]) concentrations have been measured by UV-Vis spectroscopy. The results of these experiments have been combined with a kinetic model to elucidate the primary products of the aqueous and surface reactions. The reaction of ozone with aqueous iodide has been inferred to originate different products depending on whether it occurs at the surface *via* O₃ adsorption (product I₂[−]) or in the aqueous phase *via* O₃ solvation (product IO[−]). The surface reaction of ozone with solid KI in the presence of water vapor forms KIO₃, and other species, which are likely to be gaseous. Although the reactions have been studied in aerosols, the results can be extrapolated to aqueous solutions as well.

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1. Introduction

Atmospheric iodine greatly influences tropospheric ozone and HO_x/NO_x levels and can lead to the formation of ultrafine particles.^{1–6} The main sources of atmospheric iodine are HOI and I₂ emitted upon the interaction of ozone with seawater iodide.³ Ozone reacts with iodide both in the aqueous phase, *via* O₃ solvation, and at the surface, *via* O₃ adsorption on halide ions I[−], Br[−], and Cl[−],⁷ ultimately forming volatile halogen compounds, such as hypoiodous acid (HOI) and molecular iodine (I₂).^{3,8,9}

Contrary to seawater, sea-salt aerosols are an iodine sink, instead of a source, as inferred from the high enhancement factors (EF) of iodine over neutral tracer Na⁺ (I/Na) observed in sea-salt aerosols.^{10,11} However, the uncertainty in the extent of iodine exchange between the gas phase and sea-salt aerosols has been reported to greatly influence the estimation of atmospheric iodine levels.¹² In addition, there are other gaps in the knowledge of iodine chemistry in aerosols.^{13,14} First, the direct

products of the reactions of ozone with I[−] have not been clarified,⁷ an aspect which be attempted to be elucidated in the present work. Second, iodide concentrations in marine aerosols (*e.g.* Saiz-Lopez *et al.*¹⁵) are not known with certainty, as the off-line nature of the analysis method used has been suggested to lead to formation of I[−] during sample storage, yielding systematically wrong results.¹⁴ Third, organic iodine chemistry is poorly known.^{13,16}

Ozone reacts with I[−] in aqueous media (solutions or particles) *via* several pathways:^{7,17} an aqueous-phase reaction *via* solvation of ozone,¹⁸ a Langmuir–Hinshelwood reaction *via* adsorption of ozone at the aqueous surface⁹ and, in the presence of Cl[−], an additional Langmuir–Hinshelwood reaction that is catalyzed by this halide.⁷

Although HOI is an ultimate product of the aqueous-phase reaction of ozone with I[−],³ it has not been clarified whether the reaction occurs through the intermediate IO[−] and which of the following reactions take place:^{7,19}

The product of the surface reaction of ozone with aqueous I[−] is not clear either, with some candidates having been suggested, such as IO[−], HOI, radical I, and radical I₂[−].^{7,9,20} In a previous work,⁷ the radical product I₂[−] was proposed to be formed, but there was no clear evidence for this suggestion, as

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the formation of this species in the reaction has not been detected. The main products that have been detected in previous works^{9,21,22} are the gas-phase products iodine (I_2) and HOI and the aqueous-phase products I_2 , iodate (IO_3^-), and triiodide (I_3^-).

The net non-catalytic surface reaction of ozone with I^- could be analogous to (R1) or (R2), or could be the following alternative reactions:²⁰

In addition, the product IO_2^- has been recently shown to be formed by the reaction of ozone with iodide solvated by a single H_2O molecule.²³ This finding adds greater uncertainty regarding the products of the actual reactions. However, I^- is hydrated by six H_2O molecules in the aqueous phase instead of one.²³

In the present study, aqueous KI aerosols have been exposed to ozone in a flow tube, and final I^- and IO_3^- concentrations have been determined by UV-Vis spectroscopy. Using these results and a kinetic model, we will attempt to elucidate the products of the aqueous-phase and surface reactions of ozone with I^- . As both reactions have been found to occur in seawater and to be major sources of atmospheric iodine,⁷ the elucidation of their products may help to advance the knowledge of iodine chemistry in seawater. In addition, it may contribute to increase the understanding of bromine chemistry, as both of these elements are halogens and often react in analogous manners.

Sea-salt aerosols transported inland can become dry and interact with ozone. Several studies^{24–26} using X-ray photoemission spectroscopy (XPS), atomic force microscopy (AFM), and X-ray diffraction have studied the interaction of ozone with solid KI aerosols in the absence of water vapor and have found that KIO_3 is the sole final product. The net reaction in this case has been proposed to be the following:^{24–26}

The formation of IO_3^- in solid phase has been proposed to occur through the intermediates IO^- and IO_2^- ,²⁴ as in the aqueous phase. In the presence of water vapor, $KIO_3(s)$ grown on $KI(s)$ has been found to lead to the formation of $KOH(s)$, presumably through the dissociation of H_2O followed by the Dushman reaction:^{26,27}

The simultaneous interaction of ozone and water vapor with $KI(s)$ aerosols has not been studied previously. In the present study, this interaction will be studied to investigate whether the product of the reaction of ozone with solid KI in the presence of water vapor is also KIO_3 or is a different one.

2. Material and methods

2.1. Experimental

2.1.1. Aerosol flow tube system. The experiments were carried out using a constructed aerosol flow tube system. A diagram of the aerosol flow tube system is shown in Fig. 1. The major components of the experimental system are described below.

All flows in the experiment were generated by a zero air generator (F-DGSI UZAG10—10 L min⁻¹, humidity content <0.05 ppm, particles filtration level of 0.1 μ m, water dew point of -50 °C). Aqueous KI aerosols were produced from 0.1 M KI solutions (Sigma Aldrich, $\geq 99\%$) in distilled water using a commercial constant output atomizer (TSI 3076). An impactor was used just after the atomizer with a nozzle to remove larger particles and to stabilize the aerosol flow. Aerosol particle concentration was kept approximately constant ($\pm 5\%$) during all experiments since all flows (except a small ozone flow) were kept constant, and the atomizer was cleaned between experiments nebulizing distilled water to allow a constant aerosol output.

The flow from the atomizer (~ 3.3 L min⁻¹) was mixed with dry air flow (2.7 L min⁻¹) in a conditioning glass tube (120 cm length, 1.7 cm i.d.) for a residence time of about 4 s before entering the reaction flow tube to allow time for water to achieve equilibrium between gas phase and the aerosols at the given relative humidity (RH). The dry air flow was controlled by a mass flow controller (labeled as MFC2 in Fig. 1, Tylan, FC-280).

The reaction flow tube was a vertically oriented glass tube (60 cm length, 7 cm i.d.). The aerosol flow tube was kept at ambient pressure and room temperature, where its temperature and relative humidity were monitored by a Vaisala HUMICAP[®] Humidity and Temperature Transmitter HMT337.

The aerosol flow mixed with zero air was introduced in the flow tube through a central inlet (1.2 cm i.d.), and ozone was

Fig. 1 Schematic diagram of the aerosol flow tube system. MFC = Mass Flow Controller, T = Temperature, RH = Relative Humidity.

Q5 Table 1 Description of experimental conditions for each series of experiments

Series	Estimated d_p /nm	Estimated $[KI]_p$ /M*	$V_g/V_p/10^{10}$	$S_p/V_g/10^{-4} \text{ cm}^{-1}$	$[O_3]_g$ /ppm	RH/%	$T/^\circ\text{C}$
Aqueous aerosols	80	7	1	0.8	0.07–1.1	63–66	26–29
Dry aerosols	40	>7	1	1	0.3–2.8	15–29	21–27

d_p = mean aerosol diameter; S_p/V_g = particle surface area per gas phase volume; V_g/V_p = gas to particle volume ratio. $[KI]_p$ = initial KI concentration in the aerosols.

introduced through two side ports. The total flow rate through the flow tube was in the range of 6 L min^{-1} , and the corresponding linear velocity was about 5 cm s^{-1} . The Reynolds number ($Re = \rho v D / \eta$, where ρ and η are the density, 1.2 kg m^{-3} , and dynamic viscosity, $1.8 \times 10^{-5} \text{ Pa s}$, of humid air at 27°C , respectively, v is the mean flow velocity and D is the diameter of the flow tube) was ~ 120 , indicating that the flow through the reaction flow tube was laminar (< 2100).^{28,29} Theoretical diffusional O_3 mixing time (*i.e.* $r_t^2/5D_g$)³⁰ with the aerosol flow upon exiting the inlet was $\sim 4 \text{ s}$ based on the distance from side port to the middle or the side of the flow tube ($r_t = 1.75 \text{ cm}$) and the gas-phase diffusion coefficient of ozone ($D_g = 0.14 \text{ cm}^2 \text{ s}^{-1}$).³¹ In order to evaluate whether mixing was faster than diffusion, some experiments were done substituting by colorless NO in the flow tube and, by reaction with oxygen of the air, NO_2 was formed which could be visually observed by the appearance of orange-brown color.²⁸ It was concluded that mixing was complete and that the flow was stable by $\sim 3 \text{ s}$ in the flow tube. The reaction time was fixed at 22 s in all experiments.

Ozone was generated by introducing 2.5 L min^{-1} of zero air into an ozonolyzer (EASELEC OZONE Generator ELC-5G 5 g h^{-1} for large ozone concentrations). A fraction of this flow, which was controlled by MFC4 (Tylan FC-260), was introduced into the flow tube. The ozone concentration in the stream exiting the ozonolyzer that was not introduced in the flow tube was determined by UV-Visible absorption at $\lambda = 254 \text{ nm}$ using UVIKON 930 Spectrophotometer fit with a glass cell with 10 cm long quartz windows (the cross section of ozone, σ_{O_3} , is $1.129 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$),³² and the ozone concentration in the flow tube was estimated considering the molar fraction of ozone. This estimation was checked using an UV Absorption Ozone Analyzer (SIR S-5014) and a calibration factor was applied to correct for possible wall losses in the sampling tubes.

The flow tube end was connected to two aerosol ozone denuders in series filled with active carbon ($1\text{--}4 \text{ mm}$, labkem) to eliminate ozone before aerosol sampling. Some tests were done using the UV absorption ozone analyzer to check that more than 98% of the ozone was eliminated by the denuder and a fast mobility particle sizer spectrometer was used to check that particle losses were negligible. After the denuder, a glass filter holder with a sampling diameter of 60 mm was used to collect aerosols into Whatman[®] quantitative cellulose paper filters (diameter of 90 mm and porous size of $2.5 \mu\text{m}$) during 3 min .

A study was done to determine the optimum time for aerosol sampling. Aerosol sampling time was required to be low

because the small O_3 that passed through the denuders could keep interacting with the aerosols to a significant extent. However, at the same time, this time needed to be long enough to determine I^- concentration accurately. A compromise between both premises was possible using a collection time of 3 min . Furthermore, different times were tested to ensure that the maximum KI concentration in filter extracted solutions, corresponding to zero O_3 concentration in the flow tube, was in the linear range of sampling. The KI concentration for zero ozone concentration in the filter extracted solutions was in the range of $1.4 \times 10^{-5} \text{ M}$.

Two sets of experiments were carried out. For the first set of experiments, the relative humidity was about 65%, and therefore, aerosols were in aqueous state. For the second set of experiments, the relative humidity was kept about 23%, and therefore, the aerosols were in solid state, as the efflorescence point of KI is $(38 \pm 2)\%$.³³ Typical conditions for each set of experiments are shown in Table 1. The pressure was $730\text{--}740 \text{ mmHg}$ and the total volumetric flow was 6 L min^{-1} . The aerosol diameter of the humid aerosols was estimated with previous measurements, which were done using Fast Mobility Particle Sizer Spectrometer (TSI 3091) sampling a portion of the flow that was mixed with clean air at the same RH as the sample in order to avoid saturation of the detector. The KI concentrations in the humid aerosols were calculated using an efflorescent growth factor of 1.3 g L^{-1} .³⁴ The aerosol diameter, KI concentration,³⁵ and V_p/V_g (particle to gas phase ratio) in the solid aerosols are estimated. Although these values are very uncertain, they will not be used to make any quantitative analysis. The determination of other parameters shown in Table 1 is explained in Section 1.1.4.

Immediately after collecting the aerosols for 3 min , the paper filter was transferred to a vessel that contained 25 ml of ultrapure water ($18.2 \text{ M}\Omega\text{-cm}$ obtained from an Elga Purelab Ultra Analytic water purification system) and the vessel was sonicated in an ultrasonic bath for 15 min . Several tests with variable times and variable volumes were done to check that the water volume used for the extraction, and the duration of the sonicating process were enough to allow a quantitative extraction. The extract was filtered using disposable Teflon filters Whatman Puradisc 25 TF to eliminate particles coming from the paper filters. Two different porous sizes of these filters were tested: $0.45 \mu\text{m}$ and $0.1 \mu\text{m}$ PTFE membrane, but no difference was observed.

Samples were then degassed with N_2 (Linde 5.0) to eliminate any trace of solubilized oxygen. Then they were analyzed or stored frozen in dark glass vials no more than 15 days to avoid any degradation.³⁶

2.1.2. Iodate analysis. In the present work, iodate (IO_3^-) has been determined using an optical method developed by Truesdale.^{37,38} In this method, iodate is reduced to I_2 using sulfamic acid (Sigma Aldrich $\geq 99\%$), and the resulting solution is then mixed with a concentrated solution of I^- , leading to the quantitative transformation of I_2 into tri-iodide (I_3^-). Tri-iodide is then measured spectrophotometrically at 285 nm and/or 350 nm.³⁹ In the present work, the absorption at both wavelengths were measured and calibrated with standards using an UV-Vis Spectrophotometer (Uvikon 930) with double beam. However, IO_3^- concentrations determined in the samples applying the wavelength 285 nm were systematically higher than the results using 350 nm, a difference which was attributed to the low iodate concentration of the samples, which was close to the quantification limit at 350 nm, and to the higher molar absorption coefficient of I_3^- at 285 nm. Therefore, the former wavelength (285 nm) was used to determine iodate.

Truesdale's method involves the following reactions in the forward direction:⁴⁰

Overall, each IO_3^- ion produces three HOI molecules through reactions (R8) and (R9), each of which is transformed into ion I_3^- by reactions (R10) and (R11). Thus, the signal and sensitivity of IO_3^- is tripled with respect to IO^- , HOI, or I_2 , which are transformed to I_3^- only on a 1:1 ratio.

As inferred from reactions (R8)–(R11), this method determines not only IO_3^- but the joint contribution of iodinated species with oxidation states between 0 and +5.⁴⁰ Therefore, the species that can contribute to the observed signal by this method, in addition to IO_3^- , are $\text{I}_2(\text{aq})$, $\text{I}_3^-(\text{aq})$, $\text{HOI}(\text{aq})$, $\text{IO}^-(\text{aq})$, and $\text{IO}_2^-(\text{aq})$. However, the concentration of these species is expected to be minor, because all these species are either volatile (HOI, I_2) or unstable (IO^- , IO_2^- , I_3^-) (see their volatility and reactivity in Section S.1.2 of the ESI,[†] and Section 1.2 in the present text, respectively). The most abundant species in the aerosols is believed to be IO^- , which could be present in a concentration of up to about 5% of initial iodide (see Fig. 5 in modeling section). However, hypoiodite (IO^-) is likely to transform during collection and sample dilution into I^- , IO_3^- , and volatile species (see reactions in Section 1.2), slightly distorting results (by $<5\%$).

2.1.3. Iodide analysis. Iodide was also analyzed spectroscopically, as this ion absorbs light in the UV region at about 198 nm and at about 227 nm, as it has been described in previous works (*e.g.* Souza *et al.*⁴¹). However, iodate slightly absorbs light at both of these wavelengths, and, therefore, the contribution of iodate must be subtracted to determine I^- by this method.⁴¹

In the present work, I^- and IO_3^- standards were calibrated separately using both wavelengths. However, the higher wavelength (227 nm) was selected because interferences by the filter papers (the absorption of the blank filters at 198 nm was 3.4 times higher than at 227 nm) and iodate were both lower using this wavelength.^{42,43}

The method described is not very sensitive, as the molar absorption coefficient for I^- is only $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (for comparison, the coefficient for I_3^- is $9.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and the sensitivity for IO_3^- is 3 times higher than for I_3^-). However, it is a simple and relatively fast method. Fortunately, I^- concentrations to be measured in this work are about 10 times higher than IO_3^- concentrations.

Some samples were analyzed using the cathodic stripping square-wave voltammetric method,⁴⁴ a time consuming method, and similar results were obtained.

Some filters with no aerosols (blanks) were sonicated in 25 ml of ultrapure water, and their extract analyzed by optical methods to determine their contribution to iodide and iodate signals from the paper filters. The contribution of iodide from the filter paper was smaller than 13% of the total iodide content determined in samples, whereas the contribution of iodate was nearly zero.

2.1.4. Summary of reaction conditions. The particle to gas-phase volume ratio (V_p/V_g) was estimated considering the iodide concentration determined in experiments where no O_3 was introduced in the aerosol flow tube ($[\text{I}^-]_{\text{bl}}$), the total volume flow through the tube (F_t), and the filter efficiency ($\eta_d = 0.9$, based in measurements done before and after the filter using a Fast Mobility Particle Sizer Spectrometer (TSI 3091)) for the estimated aerosol diameter, according to the following mass balance:

$$\frac{V_p}{V_g} = [\text{I}^-]_{\text{bl}} \cdot \frac{V_{\text{sol}}}{t_f} \cdot \left(W_{\text{KI}} + \frac{n_{\text{H}_2\text{O}}}{n_{\text{KI}}} W_{\text{H}_2\text{O}} \right) \cdot \frac{1}{\rho_{\text{aerosol}} F_t \eta_d} \quad (1)$$

where V_{sol} is the solution volume, t_f is the time during which aerosols are collected, W_{KI} and $W_{\text{H}_2\text{O}}$ are the molecular weight of KI and H_2O , respectively, $n_{\text{H}_2\text{O}}/n_{\text{KI}}$ is the estimated $\text{H}_2\text{O}/\text{KI}$ molar ratio in aerosols, which has been estimated taking into account the efflorescent growth diameter, and ρ_{aerosol} is the aerosol density.

2.2. Model description

A model has been developed in Kintecus software (version 6.51)⁴⁵ to describe iodine speciation and ozone consumption resulting from the interaction of ozone with pure aqueous KI nanoaerosols. The model consists of a gas phase and mono-disperse aerosols made up of three concentric layers: a thin surface layer, a thin aqueous layer, and a large aqueous layer, which consists of the remainder of the particle. The thickness of the surface layer has been selected to be 0.36 nm, as the diameter of I^- ,¹² for the purpose of modeling the surface reaction of O_3 with I^- . The thickness of the first aqueous layer has been somewhat arbitrarily selected to be 1.5 nm because the reacto-diffusive length for $[\text{I}^-]_{\text{aq}} = 0.5\text{--}7 \text{ M}$ is 1.8 to 0.5 nm. As the I^- concentration varies throughout simulation time, the

Fig. 2 Scheme of reactions occurring upon the interaction of ozone with I^- , assuming the surface and aqueous-phase reactions of O_3 with I^- form either IO^- or its conjugate acid HOI . The rate constants of the aqueous-phase reactions are shown in Table 2.

actual reacto-diffusive length for each I^- concentration is corrected in the model by using a fictitious ozone solubility in the thin aqueous layer, as explained in the ESI[†] (Section S.1.2). In the large aqueous layer, the concentration of dissolved ozone is set to be zero.

The non-radical aqueous-phase chemical reactions used in the model are shown in Fig. 2, and their kinetic rate and/or

equilibrium constants are compiled in Table 2. In addition, Fig. 2 shows the surface reaction of ozone with I^- and one of its hypothetical products (HOI). Radical reactions of iodinated species are shown in Table 3, radical reactions of oxygen species in Table S1 from the ESI[†] and gas-phase reactions in Table S2 (ESI[†]). The transport equations for ozone adsorption, diffusion of species between layers, and transport of volatile

Table 2 Aqueous-phase reactions and rate and/or equilibrium constants at room temperature included in the model

Reaction number	Reaction	Rate or equilibrium constant	Ref.
(R1)	$\text{I}^- + \text{O}_3 \rightarrow \text{IO}^- + \text{O}_2$	$k_1 = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Liu <i>et al.</i> , ¹⁸ Moreno and Baeza-Romero ⁷
(R2)	$\text{IO}^- + \text{H}^+ \leftrightarrow \text{HOI}$	$k_2 = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $K_2 = 2.51 \times 10^{10} \text{ M}^{-1}$	Paquette <i>et al.</i> ⁴⁶ Bischel and von Gunten ⁴⁷
(R3)	$\text{I}^- + \text{IO}^- \leftrightarrow \text{I}_2\text{O}_2^{2-}$	$k_3 = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $K_3 = 0.15 \text{ M}^{-1}$	Estimated (see text below) Wren <i>et al.</i> , ⁴⁸ Buxton and Mulazzani ^{49a}
(R4)	$\text{I}_2\text{O}_2^{2-} + \text{H}^+ \leftrightarrow \text{I}_2\text{OH}^-$	$k_{-4} = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $K_4 = 2.0 \times 10^{11} \text{ M}^{-1}$	Buxton and Mulazzani ⁴⁹
(R5)	$\text{I}_2\text{OH}^- \leftrightarrow \text{HOI} + \text{I}^-$	$k_5 = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $K_5 = 0.9 \text{ M}$	Buxton and Mulazzani ⁴⁹
(R6)	$\text{I}_2\text{OH}^- + \text{H}^+ \leftrightarrow \text{I}_2 + \text{H}_2\text{O}$	$k_6 = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $K_6 = 1.1 \times 10^{13} \text{ M}^{-1}$	Lengyel <i>et al.</i> ⁵⁰ Buxton and Mulazzani ^{49b}
(R7)	$\text{I}_2\text{OH}^- \leftrightarrow \text{I}_2 + \text{OH}^-$	$k_{7-} = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $K_7 = 0.023 \text{ M}$	Buxton and Mulazzani ⁴⁹
(R8)	$\text{I}^- + \text{I}_2 \leftrightarrow \text{I}_3^-$	$k_8 = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $K_8 = 729 \text{ M}^{-1}$	Lengyel <i>et al.</i> ⁵⁰ Burger and Liebhafsky ⁵¹
(R9)	$2\text{IO}^- \rightarrow \text{I}^- + \text{IO}_2^-$	$k_9 = 0.02 \text{ M}^{-1} \text{ s}^{-1}$	Truesdale ^{52c}
(R10)	$\text{IO}^- + \text{O}_3 \rightarrow \text{IO}_2^- + \text{O}_2$	$k_{10} = 1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Eigen and de Maeyer ⁵³
(R11)	$\text{IO}^- + \text{I}_2\text{O}_2^{2-} \rightarrow \text{IO}_2^- + 2\text{I}^-$	$k_{11} = 5.3 \text{ M}^{-1} \text{ s}^{-1}$	Wren <i>et al.</i> ^{48ac}
(R12)	$\text{IO}^- + \text{IO}_2^- \rightarrow \text{IO}_3^- + \text{I}^-$	$k_{12} = 0.5 \text{ M}^{-1} \text{ s}^{-1}$	Wren <i>et al.</i> ⁴⁸
(R13)	$2\text{IO}_2^- \rightarrow \text{IO}_3^- + \text{IO}^-$	$k_{13} = 0.02 \text{ M}^{-1} \text{ s}^{-1}$	Assumed based on reaction (R9) ^d
(R14)	$\text{IO}_2^- + \text{O}_3 \rightarrow \text{IO}_3^-$	$k_{14} = 100k_{10}$	
(R15)	$\text{IO}_2^- + \text{I}_2\text{O}_2^{2-} \rightarrow \text{IO}_3^- + 2\text{I}^-$	$k_{15} = 5k_{11}$	Assumed based on the work by Wren <i>et al.</i> ^{48a}
(R16)	$\text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O}(\text{l})$	$k_{16} = 1.3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ $K_{16} = 1 \times 10^{14} \text{ M}^{-2}$	Eigen and de Maeyer ⁵⁴ Harned and Owen ⁵⁵

^a The reaction formulated in the original reference involves I_2OH^- , instead of $\text{I}_2\text{O}_2^{2-}$, as a reactant. In the present work, it was changed based on Buxton and Mulazzani's work.^{49b} ^b These equilibrium constants were calculated as the product of several equilibrium constants reported by the cited authors. ^c The reported value required division by 3 in order to correct the mass-redox balance formulation of the original reference, as noted by Schmitz.^{56d} ^d The rate constant of reaction (R14) has been reported to be non-limiting with respect to the net reactions (R10) and (R14),⁴⁷ and we have used an estimation for k_{13} based on this.

Table 3 Aqueous-phase radical reactions and rate and equilibrium constants at room temperature included in the model

Reaction number	Reaction	Rate and or equilibrium constant*	Ref.
(F1)	$I_2^- \leftrightarrow I^- + I$	$k_{F1} = 6.9 \times 10^4 \text{ s}^{-1}$	Elliot ⁵⁷
(F2)	$2I_2^- \rightarrow I^- + I_3^-$	$K_{F1} = 7.8 \times 10^{-6} \text{ M}$	Mulazzani and Buxton ⁵⁸
(F3)	$I + I_2^- \rightarrow I_3^-$	$k_{F2} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
(F4)	$2I \rightarrow I_2$	$k_{F3} = 4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
(F5)	$I_2^- + OH^- \leftrightarrow HOI^- + I^-$	$k_{F4} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	
(F6)	$HOI^- \leftrightarrow I + OH^-$	$k_{F5} = 2.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Mulazzani and Buxton ⁵⁸
		$k_{-F5} = 6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	
(F7)	$I_3^- + O_2^- \rightarrow I_2^- + I^- + O_2$	$k_{F6} = 3.5 \times 10^7 \text{ s}^{-1}$	Mulazzani and Buxton ⁵⁸
(F8)	$IO^- + O_2^- + H_2O \rightarrow HOI^- + O_2 + OH^-$	$k_{-F6} = 1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	
(F9)	$IO_2^- + O_2^- + H_2O \rightarrow IO + O_2 + 2OH^-$	$k_{F7} = 2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Schwarz and Bielski ⁵⁹
(F10)	$IO_3^- + O_2^- \rightarrow IO_3^{2-} + O_2$	$k_{F8} < 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	
(F11)	$I^- + O^- + H_2O \rightarrow HOI^- + OH^-$	$k_{F9} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Sellers ⁶⁰
(F12)	$IO^- + O^- + H_2O \rightarrow IO_2^{2-} + OH^-$	$k_{F10} = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	
(F13)	$IO_2^- + O^- + H_2O \rightarrow IO_3^{2-} + OH^-$	$k_{F11} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Mulazzani and Buxton ⁵⁸
(F14)	$IO_3^- + O^- \rightarrow IO_4^{2-}$	$k_{F12} = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
(F15)	$2IO \rightarrow I_2O_2$	$k_{F13} = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Buxton and Sellers ⁶¹
(F16)	$I_2O_2 + H_2O \rightarrow HOI + IO_2^- + H^+$	$k_{F14} = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
(F17)	$I_2O_3 + H_2O \rightarrow HOI + IO_3^- + H^+$	$k_{F15} = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Buxton and Sellers ^{61 d}
(F18)	$I_2O_4 + H_2O \rightarrow IO_2^- + IO_3^- + 2H^+$	$k_{F16} = 1 \times 10^4 \text{ s}^{-1}$	
(F19)	$I_2O_5 + H_2O \rightarrow 2HOI$	$k_{F17} = 1.1 \times 10^4 \text{ s}^{-1}$	e
(F20)	$I_2O + H_2O \rightarrow 2HOI$	$k_{F18} = 1.1 \times 10^4 \text{ s}^{-1}$	
(F21)	$IO_3^{2-} + H_2O \leftrightarrow HO_3I^- + OH^-$	$k_{F19} = 1.1 \times 10^4 \text{ s}^{-1}$	e
(F22)	$IO_3^{2-} + HIO_3^- \rightarrow IO_3^- + IO_2^- + OH^-$	$k_{F20} = 1.1 \times 10^4 \text{ s}^{-1}$	
(F23)	$2IO_3^{2-} + H_2O \rightarrow IO_3^- + IO_2^- + 2OH^-$	$k_{F21} = 5.4 \times 10^9 \text{ s}^{-1}$	Buxton and Sellers ⁶¹
		$k_{-F21} = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
(F24)	$HIO_3^- + HIO_3^- \rightarrow IO_3^- + IO_2^- + H_2O$	$k_{F22} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Mezyk and Elliot ⁶³
(F25)	$2IO_2^{2-} + H_2O \rightarrow IO^- + IO_2^- + 2OH^-$	$k_{F23} = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
(F26)	$2IO_4^{2-} + H_2O \rightarrow IO_3^- + H_2IO_6^{3-}$	$K_{F23} = 20 \text{ M}$	Mezyk and Elliot ⁶³
(F27)	$2H_2IO_6^{3-} \rightarrow IO_3^- + I^{VII}I$	$k_{F24} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
(F27)	$IO_2 + H_2O \rightarrow HIO_3^- + H^+$	$k_{F25} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Estimated ^f
(F28)	$IO^- + HO_2^- \rightarrow I^- + O_2 + OH^-$	$k_{F26} = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	
(F29)	$IO_2^- + HO_2^- \rightarrow IO^- + O_2 + OH^-$	$k_{F27} = 5.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	g
(F30)	$I_2O^{2-} + HO_2^- \rightarrow 2I^- + O_2 + OH^-$	$k_{F27} = 1 \times 10^3 \text{ s}^{-1}$	
(F31)	$I_2^- + O_3^- \rightarrow 2I^- + O_3$	$k_{F28} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Burns and Marsh ⁶⁴
(F32)	$I + O_3^- \rightarrow I^- + O_3$	$k_{F29} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	
(F33)	$IO + O_3^- \rightarrow IO^- + O_3$	$k_{F30} = 1.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Estimated ⁱ
(F34)	$IO_2 + O_3^- \rightarrow IO_2^- + O_3$	$k_{F31} = 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	
(F35)	$I + O^- \rightarrow IO^-$	$k_{F32} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Estimated ^k
(F36)	$IO + O^- \rightarrow IO_2^-$	$k_{F33} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
(F37)	$IO_2 + O^- \rightarrow IO_3^-$	$k_{F34} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Estimated ^l
		$k_{F35} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
		$k_{F36} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Estimated
		$k_{F37} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	

^a The rate constant has been assumed to be the same as that of reaction $IO_3^- + CO_2^-$.⁶² ^b Estimation based on reactions (F12) and (F14). ^c The product of this reaction has been assumed. ^d The rate constant of this reaction was assumed by Buxton and Mulazzani.⁴⁹ ^e The rate constant of these reactions has been assumed to be the same as k_{F16} . The reaction products stated in the reference given are $IO_4^- + IO_3^-$, but we have included the net reaction at high pH, in which IO_4^- converts into $H_2IO_6^{3-}$. ^f Estimation based on reaction (F23). ^g The stoichiometry of product I^{VIII} was not provided in the referenced work. ^h The value of this rate constant has been assumed, as HO_2^- has been determined to react with HOI with a rate constant of $10^8 \text{ M}^{-1} \text{ s}^{-1}$.⁶⁵ ⁱ Estimation based on reaction (F28). ^j Estimated as the rate constant reported for the reaction $I_2OH^- + H_2O_2$,⁶⁶ because I_2OH^- is the conjugate acid of I_2O^{2-} . The products of the reaction have been proposed to be $IOOH$ and I^- , where $IOOH$ is reported to convert to break down in the presence of OH^- . Here, the net products at high pH have been indicated. ^k Estimation based on reaction of BrO with O_3^- . ^l Estimated based on reaction (F32).

species (e.g. O_3 , I_2 , and HOI) between the gas phase and the aqueous-phase layer are given in Section S.1 in the ESI†

In order for ozone to react with I^- in the aqueous phase, it must diffuse across the gas phase and dissolve in the aqueous phase:

where $O_3(g)$ is ozone in the gas phase bulk, $O_3(g_s)$ is gaseous ozone near the aqueous surface, and $O_3(aq)$ is dissolved or aqueous ozone. However, gas-phase diffusion of O_3 is fast

compared to accommodation of O_3 for small KI nanoparticles (see Section S.1.5 in the ESI†). Therefore, $[O_3]_{gs}$ is approximately equal to $[O_3]_g$ in the present case (Fig. 3).

As ozone reacts with I^- very fast¹⁸ and I^- concentration is very high under present conditions, the reacto-diffusive length is very short:

$$l = \sqrt{\frac{D_{aq}}{k_1[I^-]_{aq}}} \quad (2)$$

where D_{aq} is the aqueous-phase diffusion coefficient of ozone, k_1 is the rate constant of the aqueous-phase reaction $I^- + O_3$,

Fig. 3 Experimental results of the interaction of ozone with deliquesced KI aerosols for 20 s at 66% RH and 27 °C: percentage of I^- consumption (a), percentage of I^- converted to IO_3^- (b) and the final IO_3^- /others concentration ratio (c). Solid lines only show the tendency of the data.

Table 4 Parameters for the aqueous-phase reaction of ozone with I^-

Parameter	Value	Ref.
Rate constant ($k_1/M^{-1} s^{-1}$)	1.2×10^9	Liu <i>et al.</i> , ¹⁸ Moreno and Baeza-Romero ⁷
Ozone solubility in pure water ($s_0/M \text{ atm}^{-1}$)	9.7×10^{-3}	Rischbieter <i>et al.</i> ⁶⁸
Ozone solubility in aerosols ($s_{\text{aerosol}}/M \text{ atm}^{-1}$)	1.2×10^{-3}	^a
Mass accommodation coefficient (α_{aq})	0.04	Hu <i>et al.</i> , ⁶⁹ Moreno and Baeza-Romero ⁷
Diffusion coefficient of aqueous ozone ($D_{\text{aq}}/\text{cm}^2 s^{-1}$)	2.0×10^{-5}	Johnson and Davis ⁷⁰

^a This is an estimated value for the present aerosols considering the composition of the aerosol changes from 7 M KI to up to 7 M KOH as well as other factors (see Section S.1.2 in the ESI).

and $[I^-]_{\text{aq}}$ is the iodide concentration in the aqueous phase. Table 4 summarizes the values of the parameters for the aqueous-phase reaction under the present conditions. Within about 0.6 nm of depth, the iodide concentration has been experimentally determined to be 3.5 times than in the aqueous bulk for $[I^-]_{\text{aq}} = 3 \text{ M}$.⁶⁷ However, the surficial enhancement of iodide for other concentrations is unknown. Therefore, an enhancement factor of 2 has been assumed in the surface layer, which is 0.36 nm deep (see Section S.1.3 in the ESI†). The iodide enhancement in the outermost region 0.3 nm-deep of the first aqueous layer of depth has not been included for simplicity, even though this assumption may decrease the model-predicted values of iodate by up to a factor of 3. Activity coefficients have not been included because there are not available models to estimate these coefficients for mixed

solutions of high concentration. The main uncertain parameters affecting iodide conversion and iodate formation are the solubility of I_2 (40%), the accommodation coefficient of I_2 (20%), and the rate coefficient k_{F13} (15%) (see ESI†).

The aqueous-phase reactions of dissolved ozone with I^- that will be tested to model the experimental results are (R1) and (R2), which can be more specifically formulated as follows:

The surface reaction of ozone with I^- has been proposed to require the following chemical adsorption process, apart from (R12):⁷

where $\text{I}^-(\text{surf})$ is surficial iodide and $\text{OOOI}^-(\text{surf})$ is an adduct or complex formed between I^- and O_3 . As it is not known how the adduct OOOI^- reacts, the following reactions will be tested in the present model:⁷

Although the products of the surface reaction of ozone with I^- are unknown, the kinetics of this reaction have been determined.⁷ This reaction has been proposed to follow first order kinetics in $\text{OOOI}^-(\text{surf})$.⁷ The uptake coefficient for the surface reaction for $[\text{I}^-]_{\text{aq}} = 7 \text{ M}$ has been estimated to be about 0.06 using a model that fits previous studies that have been done using different I^- and O_3 concentrations.⁷ However, as determined by experimental studies,^{35,71,72} the actual coefficient for $[\text{I}^-]_{\text{aq}} = 7 \text{ M}$ is about 0.01, a discrepancy which we attributed with considerable uncertainty to the activity coefficient of surficial I^- . Our previous work was a fit for a very wide range of I^- concentrations, but only high I^- concentrations are relevant in the present work. Therefore, the experimental value of 0.01 will be used to correct the rate constant of the surface reaction determined by Moreno and Baeza-Romero⁷ (140 s^{-1}), which will be divided by 6 ($0.06/0.01$). Table 5 summarizes the parameters for the surface reaction of ozone with I^- . Other parameters related to this reaction are shown in Section S.1 of the ESI.[†]

3. Results and discussion

3.1. Interaction of O_3 with deliquesced (aqueous) KI aerosols

Fig. 2a and b show the percentage of iodide consumed, the percentage of iodide converted to iodate as a function of ozone concentration, and the final IO_3^- /other products concentration ratio. The scatter is high because the technique used for I^- is not sensitive, and because IO_3^- concentrations are low. As inferred from Fig. 2b, most I^- is converted to products different from IO_3^- . According to the reactions involved (see Fig. 2, Tables 1, 2, and Tables S1, S2 in the ESI[†]), these different products are expected to be gaseous species (HOI or I_2), as all other products apart from IO_3^- are unstable. However, if radical chemistry is involved, there could be additional gaseous products.

The different reactions of ozone with I^- that have been hypothesized to occur in the aqueous phase (R14) and (R15) and at the surface (R16)–(R19) have been included in model simulations. Table 6 shows the different combinations of these reactions and the final products predicted by the model simulations.

The only possible combinations of reactions that qualitatively agrees with the experimental results of low IO_3^- formation is (R14) + (R18) (B), (R14) + (R19) (C), and (R14) + (R20) (D). Therefore, the aqueous-phase reaction of ozone with I^- is likely to be R14, whose product is IO^- . Hypiodite (IO^-) subsequently forms IO_2^- and IO_3^- through different reactions shown in Fig. 2, Tables 1–3 and Tables S1, S2 from the ESI.[†] If both the surface and the aqueous-phase reactions formed IO^- (combination A), this species would scarcely protonate to its conjugate acid HOI due to the high aerosol pH. Initially, pH is near 7, but OH^- is generated in the reaction of concentrated I^- (about 7 M) with ozone. As pK_a of HOI is 10.4,⁴⁷ IO^- would be generated instead of HOI . The surface reaction could be (R18), (R19), or (R20), whose products are a volatile product, such as HOI (R18) or I (R20), or the precursor of a volatile species, such as I_2^- (R19).

In an experimental work⁹ where conditions used were such that the surface reaction of ozone with I^- was found to dominate ozone uptake, gaseous radical IO was detected as a product, but its yield was low ($<1\%$). The presence of a radical suggests that other radicals are present, as radicals propagate. Therefore, combinations C and D are considered as more probable than B. Furthermore, combinations C and D are supported by the Hunt *et al.*'s hypothesis²⁰ that O_3 reacts with Br^- at the surface forming Br or Br_2^- , instead of BrO^- or HOBr , because they measured higher Br_2 concentrations than expected from the aqueous-phase equilibrium between HOBr and Br_2 .⁷³ On the other hand, if B was actually the correct route, this would agree with the reported inference that H_2O behaves like a superacid at the surface,⁷⁴ but combination B is less likely according to the literature results discussed above.

Combination C is supported by the following reaction scheme inferred in our previous study⁷ for the reaction of ozone with I^- in the presence of Cl^- , where Cl^- was concluded to act as a catalyst:

Table 5 Parameters for the surface reaction of ozone with iodide

Parameter	Value	Ref.
Rate constant (k_s/s^{-1})	23	^a
Adsorption equilibrium constant of ozone ($K_{\text{O}_3}^{\text{I}^-}/\text{cm}^3 \text{ molecule}^{-1}$)	1.2×10^{-14}	Moreno and Baeza-Romero ⁷

^a See text.

Table 6 Combinations of hypothetical aqueous-phase and surface reactions of ozone with iodide and main final products predicted by model simulations. The primary product of each hypothetical reaction is indicated in parenthesis

Combination	Aqueous-phase reaction	Surface reaction	Products ^a
A	(R14) (IO^-)	(R17) (IO^-)	Only IO_3^-
B	(R14) (IO^-)	(R18) (HOI)	Mostly GS, some IO_3^-
C	(R14) (IO^-)	(R19) (I_2^-)	Mostly GS, some IO_3^-
D	(R14) (IO^-)	(R20) (I)	Mostly GS, some IO_3^-
E	(R15) (HOI)	(R17) (IO^-)	Mostly IO_3^- , some GS
F	(R15) (HOI)	(R18) (HOI)	Only GS
G	(R15) (HOI)	(R19) (I_2^-)	Only GS
H	(R15) (HOI)	(R20) (I)	Only GS

^a GS = gaseous species.

This scheme was proposed in our previous study,⁷ but an explanation was not offered. Ion I^- (surf) is more likely to react with $\text{ClO}^- \cdot \text{OO}$ than with $\text{Cl}^- \cdot \text{OOO}$ because atom Cl is less electronegative in the former compound than in the latter compound. This agrees with the existence of reactions (R21) and (R22), which have been inferred theoretically.⁷⁵

Fig. 4a and b shows I^- consumption and I^- converted into IO_3^- in deliquesced KI aerosols, as predicted by the model assuming that "C" is the right combination of reactions, along with the experimental results.

The model fit underestimates IO_3^- production and greatly overpredicts I^- consumption. The underestimation of iodate is probably due to the fact that I^- enhancement in the outermost region of the aerosols has not been fully accounted for in the model (see Section 2.2). The disagreement in iodide cannot be attributed to the uncertainty of the particle to gas ratio (V_p/V_g) nor the particle radius, since both parameters have a very small influence on model results (<1%). Decreasing the rate constant of the surface concentration of ozone with I^- by a factor of 2 would not improve the agreement much. The uncertainty in the transport coefficients of mass between aerosol layers does not have much influence over I^- consumption (see Sections S.1.3 and S.1.6 in the ESI†). Therefore, it is possible that additional surface or aqueous-phase reactions that are unknown lower I^- consumption. Another possibility could be that periodate is formed, a compound which absorbs at 222

nm^{76} and thus may interfere in the analysis of I^- , leading to an apparently higher signal of I^- . However, the I^- concentration obtained by applying the wavelength 198 nm is only about 10% different from the one obtained at 227 nm. Moreover, the periodate-forming reaction of ozone with IO_3^- has a negligible rate.¹⁹ In consequence, this interference cannot explain the differences between model and experimental results. Finally, another possibility to explain the differences could be that the iodide concentration at the surface has not been adequately estimated in the present model, where a $[\text{I}^-]_{\text{surf}}/[\text{I}^-]_{\text{aq}}$ ratio of 2 has been assumed (Section S.1.3 in the ESI†). This value has been assumed because the iodide concentration over a surface region 0.6 nm deep has been measured to be 3.5 times higher than in the aqueous phase for an iodide concentration of 3 M,⁶⁷ but the ratio $[\text{I}^-]_{\text{surf}}/[\text{I}^-]_{\text{aq}}$ might be lower for higher I^- concentrations. However, the surface concentration of iodide that is relevant in the present work is the depth equal to the iodide diameter (0.36 nm) because adsorbed ozone is unlikely to adsorb in a region deeper than this length. As iodide is unlikely to be uniformly distributed across the surface depth,⁷⁷ the relevant surface concentration of iodide could be a few units different from the assumed value. If the ratio $[\text{I}^-]_{\text{surf}}/[\text{I}^-]_{\text{aq}}$ is assumed to be 1 in the model, the model fit for I^- consumption improves, but it is still not adequate and the model fit for I^- conversion to IO_3^- worsens, as shown in Fig. S1 in the ESI.†

Fig. 4 Model-predicted iodide consumption (a) and iodide converted to iodate (b) in the interaction of O_3 with deliquesced KI aerosols for the conditions shown in Table 1 using combination of reactions C from Table 6 (R14) and (R19). Dots represent experimental data.

More reaction schemes could be proposed to explain the experimental results. For example, both the aqueous-phase and surface reactions could form HOI (combination F) and an additional surface reaction could yield an iodate precursor. Such surface reaction could involve adsorbed HOI:

However, we believe these possibilities are less likely because these reactions do not generate radicals, which were observed by Sakamoto *et al.*⁹ when a KI solution was exposed to ozone. In addition, the estimation of I^- consumption would not improve if (R24) and (R25) were assumed.

Fig. 5 shows the model-predicted evolution of the concentration of $\text{OH}^-(\text{aq})$ and the main iodinated species involved in the interaction for an O_3 concentration of 0.5 ppm assuming the same model as in Fig. 4, which is the best fit. The concentrations of the gaseous iodinated species have been multiplied by V_g/V_p in order to compare the production of these species with the production of aqueous-phase species. The main iodinated products are $\text{HOI}(\text{g})$, $\text{I}_2(\text{g})$, and $\text{IO}_3^-(\text{aq})$. In addition, some $\text{I}(\text{g})$ and $\text{I}^{\text{VII}}(\text{aq})$ are predicted to be formed. The main aqueous intermediate products are predicted to be IO^- , I_2O^{2-} and IO_2^- .

3.2. Interaction of ozone with solid KI aerosols

Fig. 6a–c show the percentage of consumed I^- , the percentage of I^- that has converted to IO_3^- , and the $[\text{IO}_3^-]/[\text{other products}]$ ratio in the sampled solid KI aerosols exposed to O_3 for about 22 s at 23% RH and 27 °C.

As in the aqueous aerosols, the major product formed is not iodate. However, in this case, the percentage of consumed I^- converted to IO_3^- is much higher, in agreement with previous reports that solid KI exposed to ozone is transformed into KIO_3 .^{24–26} As in the aqueous aerosols, products that are not IO_3^- are expected to be gaseous species, as no periodate (I^{VII}) has been detected in previous studies.^{24–26} The formation of

volatile species is expected to be related to the presence of water vapor, as Brown *et al.*²⁶ reported that KOH was formed when mixed solid salts KIO_3/KI were exposed to water vapor.²⁶ The formation of OH^- in that study indicates that volatile species (e.g. HOI or I_2) are formed, as OH^- neutralizes the I^- lost through the formation and evaporation of these volatile species, as it has been pointed out previously.^{24–26}

As explained in the introduction, solid KIO_3 has been proposed to be formed by the net reaction of solid KI with three O_3 molecules in the absence of water vapor.^{24,25} Using the uptake coefficient determined by Brown *et al.*,²⁴ we have estimated a rate constant for this reaction of $>0.25 \text{ s}^{-1}$ (see Section S.2 in the ESI†). By analogy with the reaction of ozone with I^- at an aqueous surface,⁷ ozone is expected to adsorb on I^- sites at a solid KI surface, forming the adduct $[\text{OOOI}]^-$,⁷⁵ which then transforms into other products. Therefore, the total order is expected to be one, corresponding to adsorbed ozone. However, the uptake also depends on the concentration of surficial I^- because this concentration influences the concentration of adsorbed ozone (see Section S.2 in the ESI†).

Unlike in the interaction of ozone with aqueous iodide, the intermediates IO^- and IO_2^- have not been detected in previous studies of the interaction of ozone with solid KI (without water vapor), suggesting that the reactions of ozone with IO^- and IO_2^- in solid phase could be much faster than the reaction of ozone with solid I^- .^{24–26} This agrees with the experimental finding that the reactions of O_3 with desolvated IO^- and IO_2^- are faster than the reaction of O_3 with desolvated I^- .⁷⁸ However, we cannot evaluate whether the reactions of O_3 with I^- , IO^- , and IO_2^- at the low relative humidity (RH) used by Brown *et al.*^{24–26} are the same as at the high RH in the present work, because the partial hydration of ions could change the course of reactions. In fact, it has been found I^- hydrated by a single water molecule reacts with O_3 yielding different products (I^- and IO_2^-)²³ than desolvated I^- , which yields IO^- .⁷⁸ However, the primary product of ozone with I^- solvated by six H_2O molecules (the usual number in the aqueous phase),¹² has not been directly demonstrated.

Fig. 5 Model-predicted evolution of the main (a) and minor (b) iodinated species involved in the interaction of ozone with deliquesced KI aerosols for the operation parameters shown in Table 1 and $[\text{O}_3]_{\text{gs}} = 0.5 \text{ ppm}$, as well as the evolution of OH^- .

Fig. 6 Experimental results for the interaction of ozone with solid KI aerosols during 22 s at about 27 °C and 65% RH: percentage of I^- consumption (a), percentage of I^- converted to IO_3^- (b), and the final $[IO_3^-]/[other\ products]$ ratio (c). Solid lines only to show the tendency of the data.

Volatile products in the present study may be formed by the Dushman reaction, as it was proposed to occur in the study by Brown *et al.*²⁶ The Dushman reaction requires protons, which can be generated by adsorption and dissociation of H_2O on defect sites of the mixed KI/ KIO_3 solid salt, as pointed by Brown *et al.*²⁶ Water is known to adsorb and dissociate on numerous solid surfaces, such as NaCl.⁷⁹ However, in the previous study by Brown *et al.*,²⁶ aerosols were exposed to $O_3(g)$ and $H_2O(g)$ separately. When the aerosols are exposed to both $O_3(g)$ and $H_2O(g)$ simultaneously, as in the present case, there may be additional pathways of gaseous iodine formation. Intermediates IO^- and/or IO_2^- are expected to be formed by the following reactions:

which are analogous to reactions (R10) and (R14) in the aqueous phase (see Table 2). Intermediate ions IO^- and IO_2^- could react with H^+ at the surface, forming HOI and/or HIO_2 . However, these reactions cannot be confirmed with certainty with the present data.

According to Fig. 6a, the formation of IO_3^- increases about linearly with $[O_3]_{gs}$ (R26) and (R27). In other words, iodate production is equal to a constant number, here referred as n_1 , times $[O_3]_{gs}$. According to Fig. 6c, the ratio $[IO_3^-]/[other$

products] also increases linearly with $[O_3]_{gs}$. In other words, this production ratio is equal to a constant number, here referred as n_2 , times $[O_3]_{gs}$. Dividing the previous equalities, it is deduced that volatile production is equal to a constant amount (n_2/n_1), suggesting that the formation of volatile products does not depend on $[O_3]_{gs}$. However, this does not allow to discern whether the Dushman reaction or the protonation of IO^-/IO_2^- are responsible for the formation of volatile species.

4. Conclusions

The reaction of ozone with I^- yields different products depending on whether it occurs within the aqueous phase, at an aqueous surface, or at a solid surface.

The reaction in the aqueous phase is thought to yield as primary product IO^- while the reaction at the aqueous surface yields a volatile species or the precursor of a volatile species, which is believed to be I_2^- , in agreement with our previous study.⁷ In order to conclude with certainty whether IO^- is the product of the aqueous-phase reaction of ozone with I^- , the reaction should be studied at high pH (>10.6) under conditions in which this reaction dominates (about $[I^-] < 10^{-5}$ M).⁷ As these reactions lead to gaseous emissions of iodine from seawater, the elucidation of their products might help to discover new reaction pathways involving these products (IO^- , I_2^-) or likely reaction intermediates ($IO^- \cdot OO$, I_2^-). In addition, the

formation of radical I_2^- implies many other iodine species by radical propagation are generated, such as IO, which has been reported before to be formed in the interaction of ozone with KI(s) solutions.⁹

On the other hand, the reaction at a solid KI surface exposed to high relative humidity yields IO_3^- and other species, which are likely to be gaseous species, but it could not be established in the present study whether these gaseous species are formed through the Dushman reaction or through the protonation of IO^-/IO_2^- .

The rate constant of the surface reaction of ozone with solid KI aerosols has been determined to be $>0.25\text{ s}^{-1}$.

Conflicts of interest

Q8

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