A kinetic model for ozone uptake by solutions and aqueous particles containing I⁻ and Br⁻, including seawater and sea-salt aerosol

Carolina Moreno[1], María-Teresa Baeza-Romero[1*]

[1] Escuela de Ingeniería Industrial y Aeroespacial. Universidad de Castilla-La Mancha, 45071, Toledo, Spain.

*corresponding author: mariateresa.baeza@uclm.es

Abstract

The heterogeneous interactions of gaseous ozone (O_3) with seawater and with sea-salt aerosols are known to generate volatile halogen species, which, in turn, lead to further destruction of O_3. Here, a kinetic model for the interaction of ozone (O_3) with Br⁻ and I⁻ solutions and aqueous particles has been proposed that satisfactorily explains previous literature studies about this process. Apart from the aqueous-phase reactions X⁻+O_3 (X=I,Br), the interaction also involve the surface reactions X⁻+O_3 that occur *via* O_3 adsorption on the aqueous surface. In single salt solutions and aerosols, the partial order in ozone and the total order of the surface reactions are one, but the apparent total order is second because the number of ozone sites where reaction can occur is equal to the surficial concentration of X⁻ ($[X^-]_{surf}$). In the presence of Cl⁻, the surface reactions are enhanced by a factor equal to $1+k_r^X[Cl^-]_{surf}/[X^-]_{surf}$, where $k_r^{Br^-} \approx 5$ and $k_r^{I^-} \approx 3 \cdot 10^{-4}$. Therefore, we have inferred that Cl⁻ acts as a catalyst in the surface reactions X⁻+O_3. The model has been applied to estimate ozone uptake by the reactions with these halides in/on seawater and in/on sea-salt aerosol, where it has been concluded that the Cl⁻-catalyzed surface reaction is important relative to total ozone uptake and should therefore be considered to model Y/YO (Y=I,Br,Cl) levels in the troposphere.

Introduction

The interaction of gaseous ozone (O_3) with iodide (I⁻) and bromide (Br⁻) present in seawater and sea-salt aerosols leads to halogen emissions.[1-5] Once in the troposphere, halogen compounds produce the radicals Y/YO (where Y=I, Br, Cl), which destroy ozone and have other effects.[6, 7] Ozone is an oxidant and toxic trace gas and it is the fourth most important greenhouse gas (after H_2O, CO_2, and CH_4),[8] making high levels of this species undesired in the troposphere. Surface ozone concentrations are lowest in remote marine regions (about 20 ppb) and can be several times higher in continental regions.[8] This geographic difference stems from two factors: first, anthropogenic emissions from the continents lead to O_3 formation;[9] second, Y/YO radicals destroy ozone in the marine troposphere.[7, 10, 11]

The ubiquitous presence of radicals Y/YO in the marine troposphere has been detected throughout the last three decades.[6, 12, 13] Although present in trace concentrations (pptv), they have a strong effect on O_3 levels because they destroy this oxidant species catalytically.[6, 14-16] In fact, radicals Y/YO have been found to be the second main sink of O_3 in the troposphere after photolysis.[2, 17] Apart from destroying tropospheric ozone, halogen radicals Y/YO also contribute to stratospheric ozone loss;[18-20] they influence the levels of HO_x and NO_x, thereby modifying the oxidative capacity of the atmosphere;[2, 15, 21, 22] and they act as a sink for gaseous mercury by oxidizing it.[2, 4] Additionally, iodine oxides form ultrafine particles that have the potential to act as cloud condensation nuclei (CCN), thereby influencing climate;[23-26] Br and Cl oxidize volatile organic compounds (VOCs);[27] and Br oxidizes sulphur species.[21]

The main sources of tropospheric halogen radicals Y/YO are sea-salt aerosol and sea emissions of halogenated compounds. Chloride (Cl⁻), bromide, and iodide are present in seawater in proportions of

about $5 \cdot 10^6 : 9 \cdot 10^3 : 1$, the concentration of chloride being 0.55 M.[28] These halides are also therefore present in sea-salt aerosols.[29, 30] Halides Cl^-, Br^-, and I^- can be released from seawater and from sea-salt aerosol through various biotic and abiotic pathways, one of which is the reaction of ozone with I^- and with Br^-.[1, 31]

The reaction of ozone with seawater I^- is believed to be the main source of gas-phase iodine,[1, 32] and explains the existence of high concentrations of IO in remote marine areas where biotic sources such as seaweeds are absent or scarce.[33] The inorganic interaction of ozone with I^- is heterogeneous, i.e., it involves reactants that are originally in different phases. The reaction between these reactants can occur either in the aqueous phase, via dissolution of gaseous ozone,[1, 34] or directly at the surface, via ozone adsorption.[34-40] Most inorganic emissions of iodine are believed to originate from the aqueous-phase reaction of ozone with I^- in sea,[1] but a surface reaction among these species[34-40] could also be a source. In fact, a recent atmospheric modeling study suggests that there are important sources of gas-phase iodine that are either unknown or inaccurately parametrized.[41] A recent study concluded that the contribution of the surface reaction of ozone with I^- in seawater was not important, but the precision of that study was low.[40]

The aqueous-phase reaction of ozone with I^- generates the volatile species HOI and I_2,[1, 34] which, after being emitted into the gas phase, are transformed chemically and photochemically into I/IO.[14] Thus, there is a natural feedback cycle stabilizing O_3 levels in the troposphere: when a certain stimulus increases ozone levels, the reaction $I^- + O_3$ in seawater becomes faster, leading to higher sea emissions of iodine; as a result, I/IO levels increase, leading to higher catalytic destruction of O_3 by I and compensating for the initial stimulus. Loss of O_3 through the reaction $I^- + O_3$ in seawater is minor, the major loss effect occurring through gas-phase catalytic destruction of O_3 by iodine.

Sea-salt aerosols are believed to emit IY (Y=I,Br,Cl) through the reaction of ozone with I^-, and to absorb HOI and possibly iodine oxides from the gas phase.[2] They are known to be a net sink of iodine, as inferred from the high enhancement factors *(EF)* of iodine that have been measured decades ago.[42, 43] Unlike iodine,[42, 43] bromine is usually depleted in SSA, with typical enhancement factors (*EF*) of 0.6.[44, 45] The interaction of O_3 with sea-salt aerosols (SSA) containing Br^- generates volatile Br and is known to be a major source of tropospheric Br/BrO.[4, 5, 21, 46] Recently, a modeling study has explained BrO levels by considering both SSA sources and sinks of bromine,[5] but the possible contribution of a surface reaction[3, 31, 46] on seawater has not been included so far. The aqueous-phase reaction of ozone with seawater Br^- is not a significant source of atmospheric bromine.[47]

The participation of Br^- and I^- in surface reactions with gaseous molecules implies that these ions reside close enough to the surface to be available for reaction with impinging gaseous molecules. Indeed, the halides Cl^-, Br^-, and I^- have been found to be enhanced near the surface in order of increasing size and polarizability ($I^- > Br^- > Cl^-$).[48-51] However, a surface reaction of O_3 with neither aqueous nor solid Cl^- has been found to occur.[52-54] Similarly to the reaction of O_3 with Cl^- in the aqueous phase,[55-57] the analogous surface reaction may have a very low rate constant.

From the previous discussion, it follows that it is necessary to accurately parametrize the kinetics of the reactions of O_3 with X^- (where X=I, Br) in order to improve model estimations of Y/YO (Y=I,Br,Cl) concentrations. In an earlier publication[40], we attempted to model the surface and aqueous-phase reaction contributions of the interaction of O_3 with I^- solutions and particles to ozone uptake by fitting results of previous studies. It was concluded that the aqueous-phase reaction dominates uptake at low I^- concentrations because, at low I^- concentrations, O_3 diffuses deeper into the aqueous phase due to slower consumption by reaction.[40] By contrast, at high I^- concentrations,[40] the surface reaction can dominate uptake because O_3 diffuses increasingly less into the aqueous phase because it is quickly consumed. However, at any I^- concentration, the aqueous-phase reaction dominates uptake if the O_3 concentration is sufficiently high due to surface saturation in ozone. However, the parameters in that study[40] were determined with a low level of accuracy and the model needs refinement.

The kinetics of the aqueous-phase reaction of ozone with Br⁻ have been reported as a function of temperature, Br⁻ activity, and O₃ concentration,[3, 58] while the kinetics of the surface reaction of ozone with Br⁻ have been modeled for various conditions.[3, 31] In the present study, the kinetics of the surface reaction of ozone with Br⁻ in solutions and aqueous particles will be modeled for a wider range of conditions of temperature and reactants' concentration by fitting results of previous studies, and the influence of Cl⁻ will be studied. In addition, our previous model of the interaction of O₃ with I⁻ solutions and aqueous particles will be improved using the knowledge gained in the study of the reactions with Br⁻. Finally, the ozone uptake by these reactions in seawater and in sea-salt aerosols will be estimated.

1. Model description

1.1 The resistor model for the interaction of O₃ with I⁻/Br⁻ solutions or particles

Ozone uptake by solutions and aqueous particles containing I⁻/Br⁻ will be described by means of the widely-used resistor model.[59-62] The dependent variable of this model is the uptake coefficient (γ), which reflects the gas consumption rate. Using O₃ as example, the uptake coefficient is defined by the following equation:

$$-\frac{d[O_3]_{gs}}{dt} = \frac{\gamma \, \omega \, S_p}{4} [O_3]_{gs} \tag{1}$$

where ω is the mean thermal velocity of gaseous ozone, S_p is the solution or particle surface area per gas volume, and $[O_3]_{gs}$ is the concentration of gaseous ozone *near the aqueous surface*. The concentration of gaseous ozone near the aqueous surface ($[O_3]_{gs}$) may be different from the concentration in the gas bulk ($[O_3]_g$) due to gas-phase resistance, as it is often the case in the interaction of O₃ with I⁻ solutions (e.g. Carpenter et al.[1]). If, instead of $[O_3]_{gs}$, the variable $[O_3]_g$ is used in equation 1, the uptake coefficient is referred as *apparent* or *effective* (γ_{eff}):

$$-\frac{d[O_3]_g}{dt} = \frac{\gamma_{eff} \, \omega \, S_p}{4} [O_3]_g \tag{2}$$

For the interaction of O₃ with I⁻ and Br⁻ solutions or aqueous particles, the uptake model needs to include terms for both the aqueous-phase reaction occurring between dissolved O₃ and X⁻ (where X=I or Br) and for the surface reaction occurring between adsorbed O₃ and X⁻.[31, 63] Figure 1 represents both reaction pathways. Assuming the reaction at the surface is completely parallel to the reaction in the aqueous phase, the uptake equation for the interaction of O₃ with an X⁻ solution or particle (γ^{X-}) is the following:[60]

$$\gamma^{X-} = \gamma_{aq}^{X-} + \gamma_s^{X-} \tag{3}$$

where γ_{aq}^{X-} and γ_s^{X-} are partial uptake coefficients given by the following equations:

$$\frac{1}{\gamma_{aq}^{X-}} = \frac{1}{\alpha_{aq}^{X-}} + \frac{1}{\Gamma_{aq}^{X-}} \tag{4}$$

$$\frac{1}{\gamma_s^{X-}} = \frac{1}{\alpha_{s,X-}} + \frac{1}{\Gamma_s^{X-}} \tag{5}$$

where α_{aq}^{X-} is the mass accommodation coefficient, which is the conductance of the mass accommodation process, Γ_{aq}^{X-} is the conductance of the aqueous-phase reaction X⁻+O₃, $\alpha_{s,X-}$ is a partial surface accommodation coefficient that is defined below, and Γ_s^{X-} is the conductance of the surface reaction X⁻+O₃. The coefficient $\alpha_{s,X-}$ used in equation 5 is only a fraction of the surface accommodation coefficient (α_s^{X-}) because the former corresponds to the process of adsorption onto the reacting halide X⁻, not onto any part of the surface, as proposed in the present work (see section 1.3).

For the interaction of O₃ with Br⁻ solutions/particles, reaction is slow and uptake is low (e.g. Artiglia et al.[3]). As a result, the surface reaction is parallel to the aqueous-phase reaction, the resistance of the

accommodation processes is probably negligible, and the following uptake model results from equations 3-5: [3, 31]

$$\gamma^{Br-} = \Gamma_{aq}{}^{Br-} + \Gamma_s{}^{Br-} \tag{6}$$

In the case of the interaction of ozone with I⁻ solutions/particles, uptake is high (e.g. Magi et al.[64]). Therefore, accommodation can be partially limiting and may need to be included in the uptake model, which is derived from equations 3-5:

$$\frac{1}{\gamma^{I-}} = \frac{1}{\alpha_{aq}{}^{I-}} + \frac{1}{\Gamma_{aq}{}^{I-}} + \frac{1}{\alpha_{s,I-}} + \frac{1}{\Gamma_s{}^{I-}} \tag{7}$$

This model assumes that the surface and aqueous-phase reactions of O_3 with I⁻ are parallel to each other, which may not be the case at high I⁻ concentrations (about >1 M).[40] For these higher I⁻ concentrations, which are not relevant to atmospheric conditions, this condition might not be met and a more complex model might need to be used, which is shown in section S.1 of the Supplementary Information.

The expression for the conductance of each process are given in the next section. A superindex "X-" will be used throughout the present article to indicate the halide X⁻ with which ozone interacts.
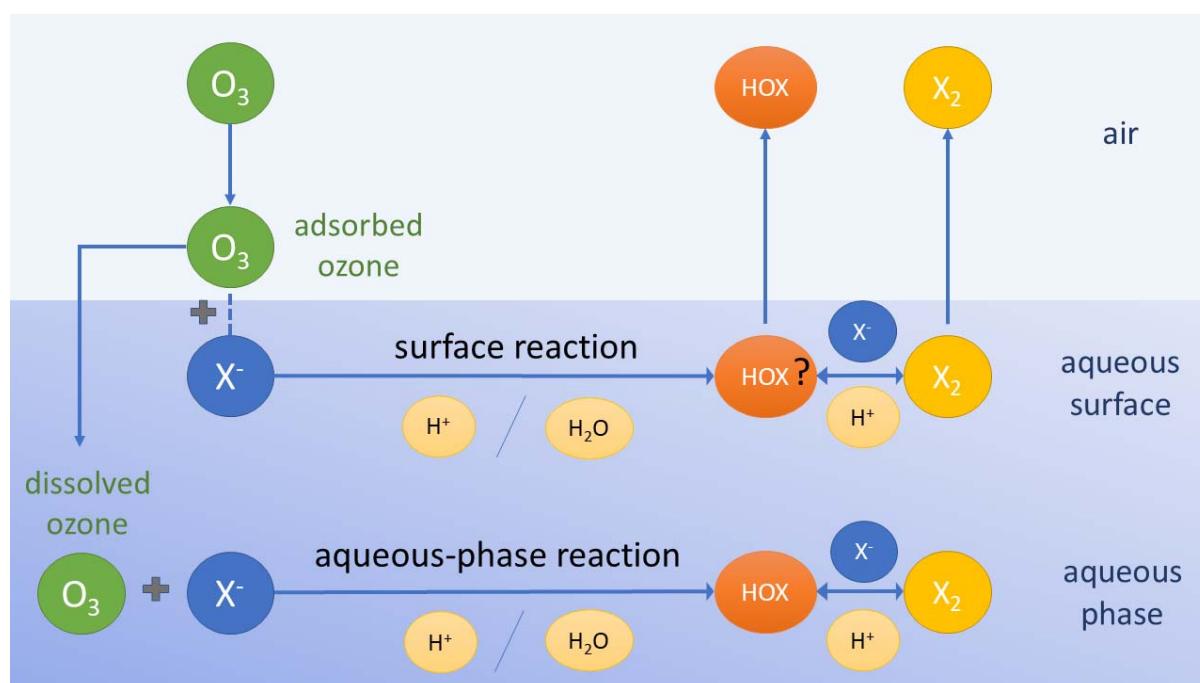

Figure 1. Known reaction pathways in the interaction of ozone with X⁻ (X=I, Br) solutions or aqueous particles: aqueous-phase and surface reactions.

1.2 Uptake by the aqueous-phase reactions X⁻+O₃ ($\gamma_{aq}{}^{X-}$)

The uptake equation for the aqueous-phase reaction X⁻+O₃(aq) will be explained in this section. In order for aqueous O_3 to react with X⁻, the following previous processes are required:

$$O_{3(g)} \leftrightarrow O_{3(gs)} \tag{R1}$$

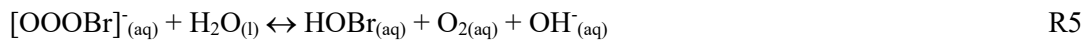$$O_{3(gs)} \leftrightarrow O_{3(aq)} \tag{R2}$$

The first process (R1) is ozone diffusion across the gas phase to the vicinity of the aqueous surface. This step is not considered in the present models (equations 6-7), as these models provide real uptake

coefficients, which refer, by definition, to $O_{3(gs)}$ concentrations. In the case of the interaction of O_3 with NaBr/KBr solutions or particles, gas-phase resistance is non-limiting in most cases because uptake is very low, and therefore $O_{3(gs)}$ is often equal to $O_{3(g)}$ in this case. In the case of I$^-$, gas-phase resistance is often significant compared to reaction and $O_{3(gs)}$ is different from $O_{3(g)}$.

The second process (R2) is mass accommodation, which involves dissolution of O_3 in the aqueous phase. The mass accommodation coefficient of ozone for water has been determined to be >0.002.[65] It will be assumed that $\alpha_{aq}^{I^-}$ is the logarithmic mean of this value and the maximum possible value of 1 (i.e., $\alpha_{aq}^{I^-}$=0.04). The uncertainty of this parameter is not very influential, because it only affects the uptake by the aqueous-phase reaction at high I$^-$ concentrations, for which the surface reaction may be dominant.[40]

The aqueous-phase reaction of O_3 with Br$^-$ has been proposed to obey the following scheme:[58]

$$O_{3(aq)} + Br^-_{(aq)} \leftrightarrow [OOOBr]^-_{(aq)} \tag{R3}$$

$$[OOOBr]^-_{(aq)} + H^+_{(aq)} \leftrightarrow HOBr_{(aq)} + O_{2(aq)} \tag{R4}$$

$$[OOOBr]^-_{(aq)} + H_2O_{(l)} \leftrightarrow HOBr_{(aq)} + O_{2(aq)} + OH^-_{(aq)} \tag{R5}$$

The existence of an intermediate adduct ([OOOBr]$^-$) in this reaction as well as in the surface reaction is supported by theoretical[58, 66, 67] and experimental works[3]. This adduct can react with H$^+$ (R4) and might react with H_2O (R5) to form the volatile product HOBr.[58] Its formation is reversible (-R3).[58] The net reaction R3-R5,

$$O_{3(aq)} + Br^-_{(aq)} + H^+_{(aq)}/H_2O_{(l)} \leftrightarrow HBrO_{(aq)} + O_{2(aq)} + (OH^-_{(aq)}) \tag{R6}$$
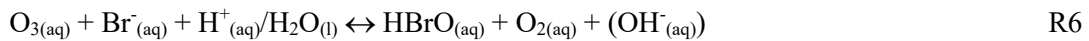
follows apparent second-order kinetics whose rate constant depends on temperature and pH (see section S.1).[3]

For the reaction of aqueous O_3 with I$^-$, an adduct has also been proposed to be formed.[34, 68, 69] This reaction has been proposed to obey the following scheme:[34, 56, 68, 70]

$$O_{3(aq)} + I^-_{(aq)} \rightarrow [OOOI]^-_{(aq)} \tag{R7}$$

$$[OOOI]^-_{(aq)} \rightarrow IO^-_{(aq)} + O_{2(aq)} \tag{R8}$$

$$IO^-_{(aq)} + H^+_{(aq)} \leftrightarrow HOI_{(aq)} \tag{R9}$$

According to a recent experimental and theoretical study[71], the schemes of reaction indicated above may require reevaluation. This new study inferred that iodide solvated by a single water molecule (I(H$_2$O)$^-$) forms IO$_2^-$, desolvated I$^-$, and other uncharacterized products of oxygen and hydrogen. However, as the authors[71] have point out, iodide is usually solvated by 6 molecules, and therefore the products of the reaction of hydrated I$^-$ with O_3 remain to be clarified.

Although not explicitly shown through the uptake models 6-7, there is an additional process, which is aqueous-phase diffusion of O_3. This process competes with the aqueous-phase reaction and therefore leads to a concentration gradient of aqueous O_3 in the direction that is perpendicular to the surface. This conductance is given by the following equation:[60, 72, 73]

$$\Gamma_{aq}^{X-} = \frac{4s\sqrt{k^{X-} \cdot a_{X-} \cdot D_{aq}}}{\omega} \cdot f^{X-} \tag{8}$$

where s is ozone solubility in non-dimensional units (aqueous molarity/ gas molarity), D_{aq} is the diffusion coefficient of aqueous ozone, ω is the mean thermal velocity of gaseous ozone, and f^{X-} is a factor (≤ 1) that is applied to particles or thin films whose radius or thickness (r_p), respectively, is small

compared to the reacto-diffusive length (l^{X-}). The mean thermal velocity of O_3 is equal to $\sqrt{8RT/\pi}$, where R is the ideal gas constant and T is temperature. The factor f^{X-} is given by the following equation:[74]

$$f^{X-} = \coth\left(\frac{r_p}{l^{X-}}\right) - \frac{l^{X-}}{r_p} \qquad (9)$$

The reacto-diffusive length (l^{X-}) is the distance from the surface of the aqueous phase at which the concentration of aqueous O_3 falls to $1/e$ of its maximum value and is given by:

$$l^{X-} = \sqrt{\frac{D_{aq}}{k^{X-} \cdot a_{X-}}} \qquad (10)$$

The rate constant for the aqueous-phase reaction $Br^- + O_3$ (k^{Br-}) has been parametrized as a function of pH and temperature by Artiglia et al.[3] (see section S.2.1 in the Supplementary Information). The rate constant of the aqueous-phase reaction $I^- + O_3$ (k^{I-}) has been determined in several studies, which have used different conditions and obtained different values ranging from $1.2 \cdot 10^9$ to $2.4 \cdot 10^9$ M^{-1} s^{-1} at ambient temperature.[47, 58, 64, 75] In the present work, the value determined by Liu et al.[58] ($1.2 \cdot 10^9$ M^{-1} s^{-1} at 25 °C) will be used because we have inferred that the conditions used by these authors are optimum for obtaining a low contribution of the surface reaction to total uptake (see section 2.3).

The temperature dependence of the rate constant for the aqueous phase reaction $I^- + O_3$ is not accurately known. Magi et al.[64] determined the rate constant at different temperature values within the range 3-20 °C and inferred an activation energy (E_a) of 73 kJ mol^{-1}. However, as explained by Moreno et al.[40], the high I^- concentrations used by Magi et al.,[64] and the enrichment of iodide later known to occur near the aqueous surface[50, 76] probably led to an inaccurate determination of the rate constant. MacDonald et al.[77] determined activation energies of -7 and +17 kJ mol^{-1} for the I_2 and HIO emissions, respectively, in the interaction of O_3 with a KI solution of concentration $1 \cdot 10^{-6}$ - $5 \cdot 10^{-6}$ M, and concluded that the activation energy of the reaction is close to zero. Therefore, a value of zero will be assumed.

Ozone solubilities (s)[78, 79] and, more weakly, aqueous-phase diffusion coefficients[80, 81] depend on the temperature and composition of the aqueous phase. The equations used to estimate these properties in the present work are shown in the Supplementary Information (sections S.2.1 and S.2.2). Activity coefficients of Br^- (γ_{Br-}), which are required to calculate the activity of Br^- ($a_{Br-} = \gamma_{Br-} \cdot [Br^-]_{aq}$), will be estimated for both single and mixed salt solutions using the thermodynamic model AIOMFAC,[82] following Artiglia et al.[3] In the case of single salt solutions of I^-, the experimental[83] activity coefficients for pure NaI and KI solutions will be used. For multicomponent solutions of I^-, the coefficients calculated for Br^- will also be used for I^-, as currently a simple method for estimating the activity coefficients of I^- has not been published.

In addition to R1-R9, several equilibrium reactions can convert aqueous HOX into X_2, X_3^-, and, in the presence of another halide, a mixed halogen species. These consecutive reactions, which are shown in Table 1, do not affect the ozone uptake, but they influence the yields of gaseous products HOX and X_2.

Table 1. Non-radical equilibrium reactions that follow after HOX or X_2 formation (X=I, Br) in the presence of Cl^-, Br^-, and/or I^-.

Equilibrium number	Reaction	Reference(s)
A1	$HOBr + Br^- + H^+ \leftrightarrow Br_2 + H_2O$	Beckwith et al.[84]
A2	$Br^- + Br_2 \leftrightarrow Br_3^-$	Hamer and Wu[83]
A3	$HBrO \leftrightarrow BrO^- + H^+$	Haag and Hoigné[85]
A4	$HOBr + Cl^- + H^+ \leftrightarrow BrCl + H_2O$	Liu et al.[58]
A5	$Br_2 + Cl^- \leftrightarrow Br_2Cl^-$	Hu et al.[65, 86] and Wang et al.[86]

A6	$BrCl + Br^- \leftrightarrow Br_2Cl^-$	Wang et al.[86]
A7	$BrCl + Cl^- \leftrightarrow BrCl_2^-$	Liu et al.[58]
A8	$HIO + I^- + H^+ \leftrightarrow I_2 + H_2O$	Eigen and Kustin[87]
A9	$I_2 + I^- \leftrightarrow I_3^-$	Lengyel et al.[88]
A10	$HIO \leftrightarrow IO^- + H^+$	Bischel and von Gunten[89]
A11	$HIO + Cl^- + H^+ \leftrightarrow ICl + H_2O$	Wang et al.[90]
A12	$I_2 + Cl^- \leftrightarrow I_2Cl^-$	Margerum et al.[91]
A13	$ICl_2^- \leftrightarrow ICl + Cl^-$	Margerum et al.[91]
A14	$ICl + I^- \leftrightarrow I_2Cl^-$	Margerum et al.[91]
A15	$HOI + Br^- + H^+ \leftrightarrow IBr + H_2O$	De Barrios Faria et al.[92]
A16	$I_2 + Br^- \leftrightarrow I^- + IBr$	De Barrios Faria et al.[92]
A17	$IBr + Br^- \leftrightarrow IBr_2^-$	Troy et al.[93]
A18	$ICl + Br^- \leftrightarrow IClBr^-$	von Glasow et al.[94]
A19	$IBr + Cl^- \leftrightarrow IBrCl^-$	von Glasow et al.[94]

1.3 Uptake by the surface reactions $O_3 + X^-$ (γ_s^{X-})

The reaction of O_3 adsorbed to an aqueous surface (here referred as $O_{3(int)}$) with aqueous X^- located at such surface ($X^-_{(surf)}$) requires the following previous processes:

$$O_{3(g)} \leftrightarrow O_{3(gs)} \qquad \qquad R1$$

$$O_{3(gs)} \leftrightarrow O_{3(int)} \qquad \qquad R10$$

where R10 represents adsorption (surface accommodation) of ozone. Because this surface reaction requires adsorption of a gaseous species to a surface, it is called Langmuir-Hinshelwood reaction.[95, 96]

While there is evidence that the surface reaction of ozone with bromide occurs via the intermediate $[BrOOO]^-$,[3] the partial order of Br^- and the reaction products of the surface reaction have not been clarified. The partial order of I^- in the surface reaction $I^- + O_3$ is believed to be 1,[34] but this order will be reexamined in the present work.

For a first-order reaction in $O_{3(int)}$ and order z in $X^-_{(surf)}$, the conductance of the surface reaction $X^- + O_3$ is given by the following equation (inferred from Ammann et al.[59]):

$$\Gamma_s^{X-} = \frac{4\,k_s^{X-}}{\omega} \frac{[O_3]_{int}}{[O_3]_{gs}} [X^-]_{surf}^z \qquad \qquad (11)$$

where k_s^{X-} is the surface reaction rate constant. The usual order of $O_{3(int)}$ in Langmuir-Hinshelwood reactions is one, as it has been shown to be the case in the reaction of ozone with Br^- (e.g. Artiglia et al.[3]) and with I^- (e.g. Sakamoto et al.[34]).

In order to model the kinetics of the surface reaction through equation 11, it is necessary to know the concentrations of $O_{3(int)}$ and $X^-_{(surf)}$ as a function of the concentrations of $O_{3(gs)}$ and $X^-_{(aq)}$, respectively. The adsorption equilibrium of ozone for a water surface may be described using a simple Langmuir model:[97, 98]

$$[O_3]_{int} = \frac{N_{O_3}^{subs} K_{O_3}^{subs} [O_3]_{gs}}{1 + K_{O_3}^{subs} [O_3]_{gs}} \qquad \qquad (12)$$

where K_{O3}^{subs} is the adsorption equilibrium constant of ozone for a surface containing a substrate where O_3 adsorbs (such as H_2O) and N_{O3}^{subs} is the total number of substrate sites for O_3 adsorption per surface area.

The adsorption equilibrium constant of ozone (K_{O3}^{subs}) for a mixed NaBr/NaCl solution at ambient temperature has been estimated to be $2 \cdot 10^{-14}$ cm^3 molecule^{-1},[31, 40] which is 40 times higher than the value of K_{O3}^{H2O} for pure water ($5 \cdot 10^{-16}$ cm^3 molecule^{-1}).[97, 98] This large difference leads to conclude that ozone adsorbs more strongly to aqueous halides than to water. Using ozone uptake coefficients obtained by Artiglia et al.[3], we have found that the value of K_{O3}^{subs} for a 0.12 M NaBr solution ($1.6 \cdot 10^{-13}$ cm^3 molecule^{-1}) is approximately the same as the value determined in another study[31] ($1 \cdot 10^{-13}$ cm^3 molecule^{-1}) where very different concentrations were used ($8.5 \cdot 10^{-3}$ M NaBr) (see section S.3.1 in the Supplementary Information). This coincidence suggests that parameter K_{O3}^{subs} required to model ozone uptake by reaction with Br$^-$ either varies little or does not vary at all with the surficial concentration of Br$^-$. This suggests that only O$_3$ adsorption on the reactive halide sites may lead to surface reaction with Br$^-$ because O$_3$ adsorbed onto Br$^-$ is strongly bound, whereas O$_3$ adsorbed onto H$_2$O has to translate across the surface to reach a bromide ion and may desorb or solvate before reaching it.

If the reaction X$^-$+O$_3$ can only occur when O$_3$ adsorbs on the respective X$^-$ ion, then the number of relevant ozone sites for the surface reaction (N_{O3}^{X-}) must be equal to the surface concentration of X$^-$. This hypothesis seems to be supported by the value of N_{O3}^{Br-} that has been estimated for a bromide solution, $2.8 \cdot 10^{12}$ molecule cm^{-2}, which is equivalent to about 0.14 M (see estimation method below), as this value is close to the aqueous bromide concentration of the solution used (0.12 M).[3] Other works using different types of solid surfaces have determined higher values of N_{O3}^{subs}: $5.7 \cdot 10^{14}$ molecule cm^{-2} on solid particles coated with a polycyclic aromatic hydrocarbon[99] and $2.4 \cdot 10^{13}$ cm^{-2} on organic matter[100]. The much higher values of N_{O3}^{subs} for these surfaces different from aqueous bromide also support the hypothesis that N_{O3}^{Br-} is limited by the concentration of Br$^-$. Therefore, in the present model, it will be assumed that the surface reaction only occurs via O$_3$ adsorption on X$^-$ sites and not on H$_2$O sites. The possibility that O$_3$ adsorption on H$_2$O sites leads to reaction will be discussed briefly in the Model Results section (2.1.3).

Replacing "subs" by "X-" equation 12, respectively, and combining equation 12 with equation 11, the following equation results for the conductance of the surface reaction X$^-$+O$_3$:[59]

$$\Gamma_s^{X-} = \frac{4\,k_s^{X-} N_{O_3}{}^{X-}}{\omega} \frac{K_{O_3}^{X-}}{(1+K_{O_3}^{X-}[O_3]_{gs})}[X^-]_{surf}^{z}$$ (13)

Finally, substituting N_{O3}^{X-}=[X$^-$]$_{surf}$ in equation 13, the following model is obtained for the surface reaction X$^-$+O$_3$:

$$\Gamma_s^{X-} = \frac{4\,k_s^{X-}}{\omega} \frac{K_{O_3}^{X-}}{(1+K_{O_3}^{X-}[O_3]_{gs})}[X^-]_{surf}^{z+1}$$ (14)

According to this hypothesis, the apparent partial order of X$^-_{(surf)}$ (z+1) is one order higher than its actual partial order (z) in the reaction.

According to this scheme, adsorption (R10) may be rewritten as the following chemical process:

O$_{3(gs)}$ + X$^-_{(surf)}$ ↔ [OOOX]$^-_{(surf)}$ R11

Chemical sorption of O$_3$ to X$^-$ is supported by the fact that the equilibrium constant K_{O3}^{X-} and the estimated adsorption energy are very high (see below). Several reactions could occur:

[OOOX]$^-_{(surf)}$ + H$^+_{(surf)}$ ↔ HOX$_{(surf)}$ + O$_{2(int)}$ R12

[OOOX]$^-_{(surf)}$ + H$_2$O$_{(surf)}$ ↔ HOX$_{(surf)}$ + O$_{2(int)}$ + OH$^-_{(surf)}$ R13

[OOOX]$^-_{(surf)}$ ↔ XO$^-_{(surf)}$ + O$_{2(int)}$ R14

[OOOX]$^-_{(surf)}$ ↔ X$_{(surf)}$ + O$_3^-{}_{(surf)}$ R15

$$[OOOX]^-_{(surf)} + X^-_{(surf)} \leftrightarrow X_2^-{}_{(surf)} + O_3^-{}_{(surf)} \qquad\qquad R16$$
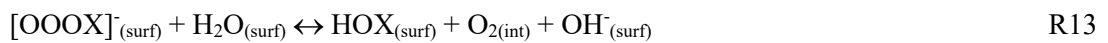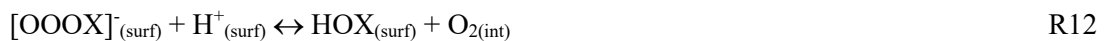
Reactions R15 and R16 were speculated by Hunt et al.[63] in order to explain the high levels of Br_2 they measured relative to consumed O_3. Under their conditions, they expected little Br_2 to be produced by possible reactions R12, R13, or R14, as the formation of Br_2 through these pathways would require equilibrium A1, which was not favored by high pH (10-11).[101] This hypothesis contrasts with the surface reaction of O_3 with I^- (R14) proposed by Sakamoto et al.[34, 1, 56] However, Sakamoto et al.[34] detected a small yield of the radical product IO (<1%), which suggests reactions R15 and R16 could be secondary reactions pathways, as these reactions form radicals which propagate, possibly forming IO. Additional reactions could be proposed considering the reactions of iodide solvated by a water molecule that have been recently found.[71]

The surficial concentration of Br^- has been suggested to follow a Langmuir relation with $[Br^-]_{aq}$ in two previous studies[36, 102] of the reaction of O_3 with Br^-. Such relation can be expressed as follows:

$$[X^-]_{surf} = [X^-]_{surf,max} \cdot \frac{K_X[X^-]_{aq}}{1+K_X[X^-]_{aq}} \qquad\qquad (15)$$

where there are two parameters, which are the maximum concentration of X^- at the surface or number of surface sites for X^- ($[X^-]_{surf,max}$) and the adsorption equilibrium constant of this halide (K_X). Parameter K_{Br} has been estimated as 1.3 and 2.8 M^{-1} in the studies[36, 102] indicated above, respectively. However, because high NaBr concentrations were used in both studies (up to 6 M), the uptake coefficients under their conditions were relatively high. Therefore, as pointed out by Clifford and Donaldson[102], gas-phase resistance may have been non-negligible in comparison to the surface reaction and the values of K_{Br} determined in these studies[36, 102] may be upper limits. The influence of gas-phase diffusion was overlooked in our previous study of the reaction of O_3 with I^-,[40] where we selected an overestimated value of K_I[35, 36].

In order to determine the parameters of equation 15, it is necessary to know $[X^-]_{surf}$ for different concentrations of $X^-_{(aq)}$. However, according to the authors' knowledge, only a couple of $Br^-_{(surf)}$ concentration values can be estimated from literature. First, the surficial concentrations of I^- and Cl^- in 3 M NaI and NaCl solutions, respectively, have been determined in a sum frequency generation (SFG) vibrational spectroscopy study to be 10.5 M and 5.5 M, respectively.[48] As Br^- is known to have intermediate propensity between Cl^- and I^-,[50] the surficial concentration of Br^- for 3 M NaBr can be estimated as the average of the surficial concentrations of I^- and Cl^- indicated above, corresponding to a $[Br^-]_{surf}/[Br^-]_{aq}$ ratio of 2.7 ± 0.9. Second, the surficial concentration of an adduct formed from $O_{3(g)}$ and $Br^-_{(surf)}$ has been determined to be $2 \cdot 10^{12}$ molecule cm^{-2} for a 0.12 M NaBr solution,[3] a value which is approximately equivalent to 0.1 M. Considering the value of $K_{O3}^{Br^-}$ we have determined (see section S.3.1 in the Supplementary Information), which implies that only 71% of the bromide sites for ozone are occupied at the ozone concentration used, the concentration of $Br^-_{(surf)}$ for a 0.12 M NaBr is estimated to be 0.14 M, corresponding to a $[Br^-]_{surf}/[Br^-]_{aq}$ ratio of 1.1.

The values of $[Br^-]_{surf}$ and $[Br^-]_{aq}$ estimated above cannot be reconciled with each other and/or with equation 15, as they would imply that the $[Br^-]_{surf}/[Br^-]_{aq}$ ratio increases with bromide concentration, contrary to surface saturation. Therefore, an average $[Br^-]_{surf}/[Br^-]_{aq}$ ratio of the two values estimated above (1.9) will be preliminarily used for all Br^- concentrations, and the model based on this assumption will be referred as "preliminary model". The relation between $[I^-]_{surf}$ and $[I^-]_{aq}$ will be estimated in the Model Results section after evaluating the model of the reaction Br^-+O_3. Although the ratios $[X^-]_{surf}/[X^-]_{aq}$ may change slightly with temperature,[103] this variation will not be considered because there are not sufficient data to estimate such variation.

The temperature dependence of $K_{O3}^{X^-}$ can be estimated by the following equation (see section S.3.2 in the Supplementary Information):

$$K_{O_3}{}^{X-} = C^{X-} \cdot \exp\left(\frac{-\Delta H_{ads}^{X-}}{RT}\right) \tag{16}$$

The parameters C^{X-} and $\Delta H_{ads}{}^{X-}$ for Br$^-$ have been estimated to be $C^{Br-}=2.0 \cdot 10^{-26}$ cm^3 molecule^{-1} and $\Delta H_{ads}{}^{Br-}=-67$ kJ mol^{-1} for the temperature range of interest in the Supplementary Information (section S.3.2). The high value of $|\Delta H_{ads}{}^{Br-}|$ (>50 kJ mol^{-1}) indicates that ozone adsorption onto Br$^-$ is chemical.[104] The adsorption equilibrium constant of ozone for iodide ($K_{O3}{}^{I-}$) will be determined in the Model Results section using kinetic results[34] of the interaction of ozone with I$^-$ solutions. The surface reaction rate constants ($k_s{}^{X-}$) will be determined in the next section based on reported results[3, 34] of O$_3$ uptake by X$^-$ solutions.

Although our previous study[40] of the interaction of ozone with I$^-$ solution/particles was able to explain which of the reactions, surface or aqueous-phase, is dominant in most previous studies, the estimation of the uptake coefficients for this interaction needs to be improved by correcting several assumptions that were made. First, the previous model assumed a constant number of surface sites for ozone. As explained above, it is more reasonable to assume $N_{O3}{}^{X-}$ is equal to the surface concentration of the halide is reacting with (in this case, I$^-$). Second, analogously as $K_{O3}{}^{Br-}$, the adsorption equilibrium constant of ozone for equation 14 ($K_{O3}{}^{I-}$) should not be assumed to vary with the surface concentration of I$^-$. Third, the estimation of the value of the adsorption equilibrium constant of iodide (K_I) must be corrected. Finally, the partial order of I$^-_{(surf)}$ assumed in the previous study[40] will be reevaluated.

Conventionally, the surface accommodation coefficient ($\alpha_s{}^{X-}$) is defined as the number of reactive gas species-surface collisions that lead to adsorption over the number of reactive gas species-surface collisions. However, according to the surface reaction scheme described above, the relevant accommodation coefficient to model the surface reactions X$^-$+O$_3$ is the number of ozone-surface collisions leading to adsorption onto the reacting halide X$^-$, not onto any part of the surface, over the number of ozone-surface collisions. Therefore, this coefficient, which will be called $\alpha_{s,X-}$ (as opposed to $\alpha_s{}^{X-}$) in the present work, is expected to be proportional to the surface concentration of the halide:

$$\alpha_{s,X-} = p^{X-}[X^-]_{surf} \tag{17}$$

where p^{X-} is a constant which, according to the definition of $\alpha_{s,X-}$ given above, can be described as follows:

$$p^{X-} = \frac{\alpha_{s,max}^{X-}}{[X^-]_{surf,upper}} \tag{18}$$

where $\alpha_{s,max}{}^{X-}$ is the surface accommodation of O$_3$ for a hypothetical surface completely covered by X$^-$, whose concentration is referred as $[X^-]_{surf,upper}$. Considering the radii of hydrated I$^-$ and Br$^-$ are both about 0.35 nm[105] and assuming that a low packing efficiency of iodide (50%) is enough for O$_3$ not to adsorb on any H$_2$O molecules (adsorption onto I$^-$ is much more favorable), $[X^-]_{surf,upper} \approx 36$ M.

An estimation of $\alpha_{s,max}{}^{I-}$ can be made by analyzing results of I$^-$ oxidation by O$_3$. In our previous work,[40] where literature results were analyzed, it was inferred that the surface reaction of ozone with I$^-$ dominates uptake at supermolar concentrations of I$^-$, unless O$_3$ was exceedingly high, a conclusion which apparently disagrees with the conclusion by a couple of works[64, 106] that the aqueous-phase reaction was dominant under those conditions. The present model also predicts that the surface reaction dominates under those conditions (see Model Results section). In addition, the present model predicts that the uptake coefficient by the surface reactions X$^-$+O$_3$ is proportional to $[X^-]_{surf}{}^{z+1}$, even in the presence of limitation by accommodation:

$$\frac{1}{\gamma_s{}^{X-}} = \frac{1}{[X^-]_{surf}{}^{z+1}}\left(\frac{1}{p^{X-}} + \frac{\omega\,(1+K_{O_3}^{X-}\,[O_3]_{gs})}{4\,k_s{}^{X-}\,K_{O_3}^{X-}}\right) \tag{19}$$

where equation 17 has been substituted into equation 14. A lower limit of p^{I-} can be inferred from uptake coefficients obtained for the interaction of ozone with I^- solutions/particles. From equations 18 and 19, it follows that $p^{I-} \geq \gamma_s^{I-}/[I^-]_{surf}$. The variable γ_s^{I-} can be obtained from determinations of γ^{I-} [64, 106, 107] by subtracting the contribution γ_{aq}^{I-} (equation 3). Although $[I^-]_{surf}$ is known only for $[I^-]_{aq}=3$ M, estimations can be made for concentrations near this value. Using uptake coefficients determined for $[I^-]_{aq}=3$ M (unknown $[O_3]_{gs}$)[64] and for $[I^-]_{aq}=7$ M (0.1 ppm $O_{3(gs)}$)[106], a minimum p^{I-} value of $1 \cdot 10^{-3}$ M^{-1} is estimated for both cases.

An upper limit of p^{I-} can be estimated using geometric considerations, as for a surface that is nearly full of I^- the value $\alpha_{s,I-}$ cannot exceed 1. Considering such surface contains a hypothetical $X^-_{(surf)}$ concentration of 36 M, the upper limit is estimated to be $2.8 \cdot 10^{-2}$ M^{-1}. Therefore, the logarithmic mean value of p^{I-} is $5 \cdot 10^{-3}$ M^{-1}.

2. Model results

2.1 Analysis of previous studies of the interaction of O_3 with Br^- solutions or aqueous particles

In this section, kinetic results that have been reported in previous studies will be analyzed to obtain the kinetic law equation for the surface reaction $Br^-_{(surf)}+O_{3(int)}$. Table 2 summarizes experimental conditions used in previous studies of the interaction of ozone with bromide. The interaction of ozone with Br^- solutions or aqueous particles has been studied by measuring O_3 uptake,[3, 58, 108, 109] Br_2 emissions,[31, 46] Br^- concentration and pH,[110] and surface-specific signals[36, 102, 111] using Br^- concentrations from $5 \cdot 10^{-4}$ to 6 M and O_3 concentrations from 0.1 to 300 ppm at different temperatures (mostly 0-25 °C), and at different pH units (1-11),[3, 63, 101] both in pure NaBr/KBr aqueous media and in the presence of other inorganic species, such as NaCl[3, 31, 46, 110, 112] and of organic substances[102, 108, 109]. Most studies were done using solutions or thin films[3, 46, 109], while a few studies employed aerosols.[63, 101, 113-115] In addition, theoretical studies have been done.[3, 58, 67, 116]

2.1.1. Determination of the kinetic law of the surface reaction $Br^-_{(surf)}+O_{3(int)}$

The rate constant (k_s^{Br-}) of the surface reaction $Br^-_{(surf)}+O_{3(int)}$ will be determined for 0° C and for 5 °C by fitting the uptake coefficients obtained by Artiglia et al.[3] for pure 0.125 M NaBr films to the present model through minimization of the residual sum of squares assuming the partial order of Br^- (z) is either 0 or 1. Figure 2 shows that the model fits the results obtained by Artiglia et al.[3] well. However, a slight systematic deviation can be detected, since the experimental uptake coefficients seem to plateau at a lower O_3 concentration than estimated by the model (see errors in Figure S2 in the Supplementary Information). This deviation cannot be corrected by changing any of the surface reaction parameters and may suggest that a simple Langmuir isotherm (equation 12) does not accurately describe the dependence of this surface reaction on the ozone concentration, and that a two-site Langmuir adsorption for ozone may be required (see section 2.1.3).
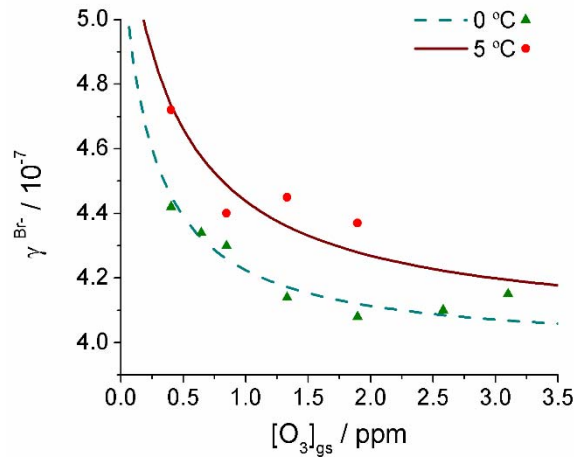
Figure 2. Uptake coefficients in the interaction of O_3 with a 0.125 M NaBr film at different temperatures: experimental values by Artiglia et al.[3] (squares and triangles) and values estimated by the "preliminary model" using the optimum values of k_s^{Br-} for each temperature (lines). Note: the assumed reaction order of $Br^-_{(surf)}$ does not influence the uptake coefficient in this case because $[Br^-]_{aq}$ is constant and k_s^{Br-} has been fit.

The values of k_s^{Br-} determined can be used to obtain the Arrhenius parameters for each assumed reaction order according to the Arrhenius equation:

$$k_s^{X-} = k_{s,0}^{X-} \cdot \exp\left(-\frac{E_a^{X-}}{RT}\right) \tag{20}$$

where E_a^{X-} is the activation energy of the surface reaction $X^-_{(surf)}+O_{3(int)}$ and $k_{s,0}^{X-}$ is the preexponential factor. The resulting activation energy of the reaction $Br^-_{(surf)}+O_{3(int)}$ is 78 ± 20 kJ mol^{-1}, which is of the same order than that of the aqueous-phase reaction (53.9 kJ mol^{-1}).[3] The preexponential factor depends on the assumed value of the partial order of $Br^-_{(surf)}$ (z). Although the Arrhenius equation parameters obtained here are not very accurate because the difference in temperature among the two datasets that have been used to determine them is small (5 °C), there are no more kinetic data available at the same Br^- concentration, according to the authors' knowledge. The rate constant k_s^{Br-} need to be determined at different temperature using results for which the same Br^- concentration is maintained, as otherwise the uncertainty in the surficial concentration of Br^- would affect the accuracy of E_a^{Br-}.

The accommodation coefficient $\alpha_{s,Br-}$ has been varied in the model to study its influence on the uptake. As it was expected,[3] this coefficient does not limit the uptake.

As the model-estimated uptake coefficients shown in Figure 2 do not depend on the assumed partial order of Br^- because $[Br^-]_{aq}$ is constant for that figure, this partial order will be evaluated using results that have been obtained at different Br^- concentrations. Lee et al.[108] measured O_3 uptake coefficients for pure 0.03-1 M NaBr solutions and different O_3 concentrations at 15.7 °C. As they reported a high level of uncertainty in their coefficients at low O_3 concentration, only the results for the highest O_3 concentration they used (1.8 ppm) will be analyzed here. This figure shows the total uptake coefficients predicted by the present model for different partial orders in $Br^-_{(surf)}$ in the surface reaction. Clearly, the model that assumes a partial order of 0 fits the results more closely. However, even this model seems to slightly overestimate the uptake coefficients at high $Br^-_{(aq)}$ concentrations (>0.1 M).
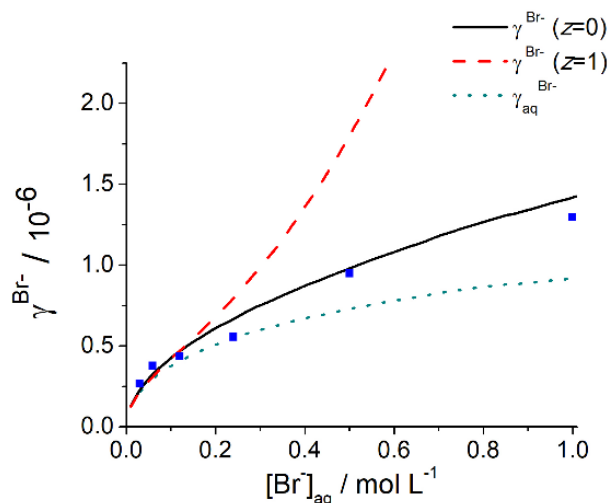
Figure 3. Uptake coefficients for the ozone interaction with pure NaBr solutions for $[O_3]_g$=1.8 ppm: experimental values obtained by Lee et al.[108] (squares) and values estimated by the "preliminary model" assuming the partial order of $[Br^-]_{surf}$ in the surface reaction (*z*) is 0 or 1, or assuming that only the aqueous-phase reaction takes place ($\gamma_{aq}^{Br^-}$) (lines).

Hunt et al.[63] measured O_3 consumption and Br_2 formation in the interaction of O_3 (0.3-1.6 ppm) with deliquesced NaBr nano-aerosols at 25 °C. The authors concluded that a surface reaction takes place under their conditions, as their results could not be explained by aqueous-phase chemistry alone. For $[Br^-]_{aq}$=5.9 M, $[O_3]_{gs}$=1.5 ppm, and r_p=285 nm, they inferred an uptake coefficient by the surface reaction of $2.3 \cdot 10^{-6}$.[114] For these conditions, the uptake coefficient estimated for the aqueous-phase reaction by the "preliminary model" is only $3.1 \cdot 10^{-8}$. The uptake coefficient estimated for the surface reaction by the model assuming *z*=0 is only a factor of 2.5 higher than the experimental one, whereas the uptake coefficient estimated assuming *z*=1 is orders of magnitude higher. Therefore, the partial order of the surface reaction in $Br^-_{(surf)}$ is concluded to be 0.

The "preliminary model" overestimates the uptake coefficients for both Hunt et al.'s study[114] and Lee et al.'s study[108]. The estimated disagreement in the surface reaction rate is 43% for 1 M at 16 °C for Lee et al.'s study[108] and 150% for 5.9 M at 25 °C for Hunt et al.'s study[63]. The disagreement suggests that either the ratio $[Br^-]_{surf}/[Br^-]_{aq}$ decreases when $[Br^-]_{aq}$ increases, instead of being constant, or that the surface reaction rate constant at high temperature has been overestimated. It will be assumed, with considerable uncertainty, that the reason for the disagreement is not an accurate value of $k_s^{Br^-}$ at ambient temperature, and a Langmuir model of adsorption for Br^- will be invoked to explain the model error. An adsorption equilibrium constant of bromide (K_{Br}) of 0.4 M^{-1} (see equation 15) explains the coefficients obtained by Hunt et al.[63] and Lee et al.'s results[108] adequately. However, the large uncertainty in $k_s^{Br^-}$ makes the estimation of K_{Br} very inaccurate, and this parameter is concluded to be between 0 and 1.3 M^{-1}, a value determined[36] in the presence of gas-phase resistance.

Using K_{Br}=0.4 M^{-1} and the ratio $[Br^-]_{surf}/[Br^-]_{aq}$=2.7 estimated for $[Br^-]_{aq}$=3 M (see Model Description section),[48] the parameter $[Br^-]_{surf,max}$ is estimated as 15 M using equation 15. Using these parameters, the parameter $k_{s,0}^{Br^-}$ for a total reaction order of 1 can be redetermined using Artiglia et al.'s results[3] as explained above, yielding $3.5 \cdot 10^{11}$ s^{-1}. All parameters related to the surface reaction $Br^- + O_3$ for pure NaBr/KBr solutions or particles obtained in the present work are summarized in Table 3.

The kinetic equation that adequately describes the uptake of the surface reaction of O_3 with Br^- in pure NaBr/KBr solutions or aqueous particles is obtained by substituting *z*=0, equation 15, and parameters from Table 3 in equation 14:

$$\gamma_s^{Br^-} = \Gamma_s^{Br^-} = \frac{4k_s^{Br^-}[Br^-]_{surf,max}}{\omega} \frac{K_{O_3}^{Br^-}}{(1+K_{O_3}^{Br^-}[O_3]_{gs})} \frac{K_{Br}[Br^-]_{aq}}{1+K_{Br}[Br^-]_{aq}} \tag{21}$$

where K_{O3}^{Br-} is given by equation 16. The model whose γ_s^{Br-} is described by equation 21 will be referred as "only Br^- model" throughout the rest of this paper, even though the presence of cations and other anions is considered to calculate several properties, such as the ozone solubility.

Table 3. Summary of parameters to model ozone uptake by the surface reaction of O_3 with Br^- (equation 21).

Parameter	Value	Estimated error or range
E_a^{Br-} / kJ mol^{-1}	78	±20
$k_{s,0}^{Br-}$ / s^{-1} [a]	$3.5 \cdot 10^{11}$	$(1.8 \cdot 10^8, 5.2 \cdot 10^{15})$
K_{Br} / M^{-1} [b,c]	0.4	(0, 1.3)
$[Br^-]_{surf,max}$ / M [b,d]	15	(8, 36)
C^{Br-} / cm^3 molecule^{-1} [e]	$2.0 \cdot 10^{-26}$	$(4.1 \cdot 10^{-27}, 1.1 \cdot 10^{-25})$
ΔH_{ads}^{Br-} / kJ mol^{-1} [e]	-67	±4

[a]The error of this parameter has been estimated considering as E_a^{Br-} as the only source, but parameters of equation 15 are also sources of error.
[b]These parameters describe the ratio $[Br^-]_{surf}/[Br^-]_{aq}$ for pure NaBr and KBr solutions or particles. However, these ratios can change in the presence of other species (see text).
[c]The lower limit of this parameter for any Langmuir isotherm is 0.[117] The upper limit of this parameter for Br^- is estimated as the value determined by Wren et al.[36] in the presence of resistance to gas-phase diffusion.
[d]The lower limit of this parameter has been estimated as the estimated surface concentration of Br^- for $[Br^-]_{aq}=3$ M (see Model Description section). The upper limit has been estimated as the maximum geometric capacity by considering the radius of hydrated bromide (0.34 nm)[105].
[e]The sources of error for these parameters are explained in section 3.2 of the Supplementary Information.

2.1.2. Study of the influence of Cl$^-$ on the surface reaction

In this section, the "only Br^- model" inferred above, which describes the ozone uptake by its interaction with pure NaBr/KBr solutions, films, or aerosols, will be applied to kinetic results[3, 31, 110] that were obtained using solutions or films that contained Cl$^-$ in addition to NaBr or KBr in order to evaluate the influence of Cl$^-$.

Using an ion-sensitive electrode and ion chromatography, Disselkamp et al.[110] monitored the evolution of H$^+$, Br$^-$, and trace ion concentrations in solutions containing $(1-12) \cdot 10^{-3}$ M NaBr and/or 2 M NaCl exposed to 15-32 ppm O_3 (at pH =3-4 at 17 °C). The main variable they reported was the rate of pH variation, which is expected to be proportional to the uptake coefficient because the main products formed (Br_2 and BrCl) consume a constant number of H$^+$ molecules per consumed O_3 molecules (2 H$^+$/O_3). For equal $[Br^-]_{aq}$, the determined rate of pH variation was up to 3.2 times higher for the mixed NaCl/NaBr salt solutions than for pure NaBr solutions. This suggests that Cl$^-$ plays a role in the surface reaction of ozone with bromide, as the aqueous-phase reaction of O_3 with Cl$^-$ is negligible[56, 57] and no evidence has been found that a significant reaction of O_3 with Cl$^-$ occurs at the surface of pure NaCl solutions[52] nor NaCl powders[54].

Several data obtained by Disselkamp et al.[110] provide evidence of the reaction pathways that are dominant under their conditions. The pH variation rate obtained for pure NaBr solutions scarcely changed with O_3 concentration from 15 to 32 ppm, clearly suggesting aqueous-phase reaction dominance for these cases (as equation 8 shows, uptake by the aqueous-phase reaction does not depend on the O_3 concentration), in agreement with the prediction of the present model for the conditions used by the authors[110]. For mixed NaBr/NaCl solutions containing $[Br^-]_{aq}=(3.9-12) \cdot 10^{-3}$ M, the pH variation rate measured by Disselkamp et al.[110] was higher by a factor of 2.7-3.2 than for the pure NaBr solutions containing the same Br$^-$ concentration. In order for the uptake estimated by the "only Br^- model" to be

reconciled with these ratios, it would be necessary to increase the model-estimated surface reaction rate by a factor of 480-1100, suggesting that ion Cl^- somehow enhances the surface reaction. This factor is within the same order of magnitude as the Cl^-/Br^- concentration ratio (170-510).

In other studies[3, 31], an extreme enhancement of the surface reaction rate can also be inferred. For example, Oldridge and Abbatt[31], who measured Br_2 formed by the interaction of ozone with solutions containing $8.5 \cdot 10^{-3}$ M KBr, 0.55 M NaCl, and 0.01 M HCl at 0 °C, obtained Br_2 emission coefficients up to 6 times higher than those estimated by the present model. As shown in Figure 4, a surface reaction rate enhancement of 150 with respect to the present model is required to fit their results. As in the study by Disselkamp et al.[110], the enhancement factor is within the same order of magnitude as the Cl^-/Br^- ratio used (65).
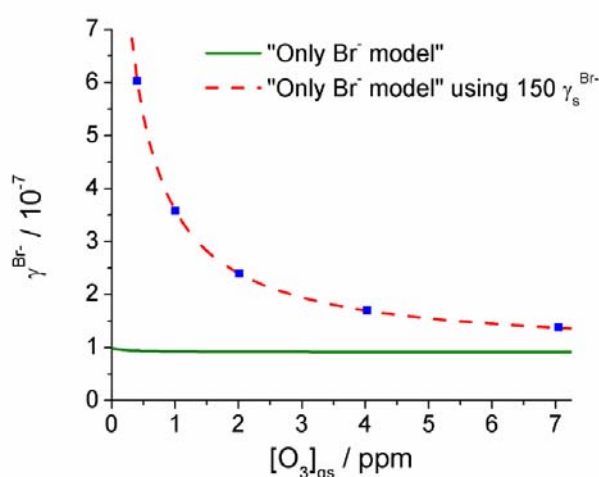

Figure 4. Uptake coefficients in the interaction of O_3 with an aqueous solution containing $8.5 \cdot 10^{-3}$ M KBr, 0.55 M NaCl, and 0.01 M HCl at 0 °C: values determined by Oldridge and Abbatt.[31] (squares) and values estimated by the "only Br^- model" and by the same model assuming the surface reaction rate is 150 times higher (lines). Note: Oldridge and Abbatt[31] determined Br_2 emission coefficients instead of O_3 uptake coefficients, but these are expected to be equal to each other under their conditions due to equilibria shown in Table 1.

Two additional datasets of uptake coefficients, which were obtained by Artiglia et al.[3], can be used to study the influence of Cl^-. As shown in Figure 5, for the interaction of ozone with a film containing 0.12 M NaBr and 0.1 M HCl, which corresponds to a Cl^-/Br^- ratio of 0.8, the model error is minimized by increasing the surface reaction rate by 2.9 times. By contrast, for a film containing 0.24 M NaBr and 0.1 M HCl, which corresponds to a lower Cl^-/Br^- ratio (0.4), the surface reaction rate seems to slightly decrease (by 10%) instead of increasing (see Figure 6). However, the latter variation might be too small (0.9) to be considered significant and is also of the same order of magnitude as the Cl^-/Br^- ratio, in agreement with the model.
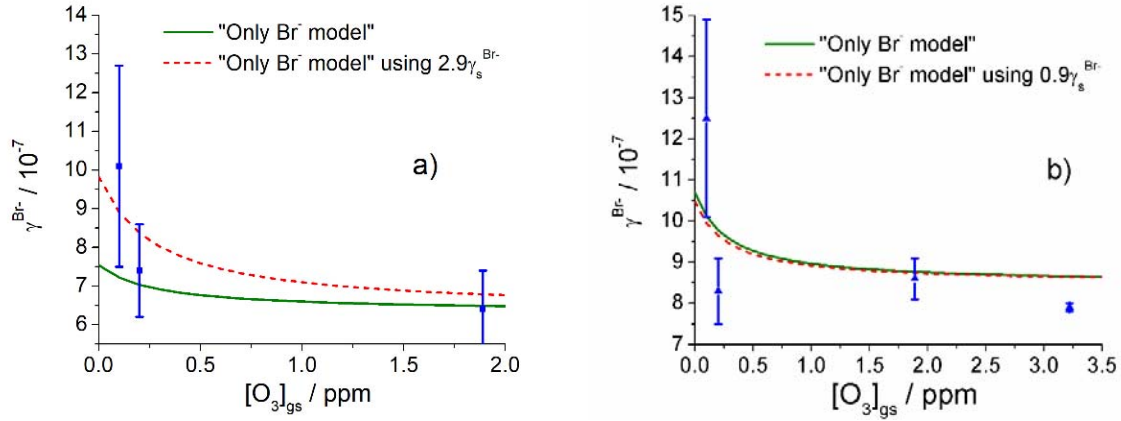
Figure 5. Uptake coefficients for the interaction of O_3 with films containing 0.12 M NaBr (a) or 0.24 M NaBr (b) in addition to 0.1 M HCl: values determined by Artiglia et al.[3] (squares) and values estimated by the "only Br⁻ model" and by a model assuming a higher surface reaction rate (lines).

The results shown above strongly suggest that the presence of Cl⁻ leads to an enhancement in the surface reaction rate that is approximately proportional to the [Cl⁻]/[Br⁻] ratio. The influence of Cl⁻ could occur through an increase in the surface concentration of Br⁻ or through the involvement of this halide as a reactant. However, the first effect would imply extremely high [Br⁻]$_{surf}$/[Br⁻]$_{aq}$ ratios (>1000), which have not been reported in any previous studies,[118-121] which have found rather moderate effects. According to the authors' knowledge, only one work[66] has reported an extreme effect, predicting that surficial I⁻ and Br⁻ are enhanced by an extreme factor (~100) in aqueous slabs of net composition of 0.9 M NaCl + 0.1 M NaI + 0.1 M NaI, but this work is theoretical.

The previous discussion suggests that Cl⁻ participates in the surface reaction of ozone with Br⁻. As it has been found that the surface reaction rate is estimated to increase in an approximately proportional manner to [Cl⁻]/[Br⁻] in the presence of Cl⁻, the uptake equation 14 for the surface reaction of O_3 with Br⁻, where z=0, must be multiplied by $1+k_r^{Br-}[Cl^-]_{surf}/[Br^-]_{surf}$ where [Cl⁻]$_{surf}$ is the surficial concentration of Cl⁻ and k_r^{Br-} is the proportionality factor:

$$\gamma_s^{Br-} = \frac{4k_s^{Br-}}{\omega}\frac{K_{O_3}^{Br-}}{(1+K_{O_3}^{Br-}[O_3]_{gs})}\left([Br^-]_{surf} + k_r^{Br-}[Cl^-]_{surf}\right) \tag{22}$$

Assuming that the surficial concentrations of Cl⁻ and Br⁻ are described by Langmuir isotherms (equation 15), the following equation is obtained:

$$\gamma_s^{Br-} = \frac{4k_s^{Br-}}{\omega}\frac{K_{O_3}^{Br-}}{(1+K_{O_3}^{Br-}[O_3]_{gs})}\left(\frac{K_{Br}[Br^-]_{aq}[Br^-]_{surf,max}}{1+K_{Br}[Br^-]_{aq}} + k_r^{Br-}\frac{K_{Cl}[Cl^-]_{aq}[Cl^-]_{surf,max}}{1+K_{Cl}[Cl^-]_{aq}}\right) \tag{23}$$

The model where γ_s^{Br-} is described by equation 23 will be referred as "mixed Br⁻/Cl⁻ model" (compare with equation 21).

The adsorption equilibrium constant of chloride (K_{Cl}) is unknown, but it is unlikely to be greater than K_{Br} because Cl⁻ has less surface propensity than Br⁻ (e.g. Jungwirth and Tobias[50]). Therefore, the estimated value of K_{Br} (0.4 M⁻¹) will be assumed, which has a wide uncertainty range ($0.4^{+0.9}_{-0.4}$ M⁻¹). However, no results have been found in literature to obtain a better estimation. Using the reported[48] ratio [Cl⁻]$_{surf}$/[Cl⁻]$_{aq}$ for [Cl⁻]$_{aq}$=3 M and the estimated value of K_{Cl} in equation 15, parameter [Cl⁻]$_{surf,max}$ is estimated to be 10 M with much uncertainty.

The parameter k_r^{Br-} will be estimated considering the values that fit all the datasets referred to above where [Cl⁻]$_{aq}$/[Br⁻]$_{aq}$>0.7, so that the effect of Cl⁻ can be quantified with enough sensitivity. The individual values of k_r^{Br-} obtained for each dataset are shown in Table 4. The dispersion in the individual

values of k_r^{Br-} is likely due to the temperature used in each study (0-17 °C) and possibly also to uncertainties in the surficial concentrations of Cl^- and Br^- in mixed salt solutions, which may depend on the proportions of Cl^-, Br^-, Na^+, K^+, H^+, and other species.[34, 119, 122] As inferred from Table 4, parameter k_r^{Br-} may correlate positively with temperature, with average values of 3.8 at 0 °C and 5.5 at 17 °C. Assuming k_r^{Br-} depends only on temperature and follows an Arrhenius equation, the estimated activation energy ($E_{a,r}^{Br-}$) and the preexponential factor ($k_{0,r}^{Br-}$) of its corresponding reaction are shown in Table 5, which compiles the parameter values required for equation 23. No correlation has been found in the present study between k_r^{Br-} and pH nor between k_r^{Br-} and the ratios $[H^+]/[Br^-]$ and $[H^+]/[Cl^-]$.

Table 4. Values of parameter k_r^{Br-} obtained using several kinetic results where different Br^-, Cl^- and H^+ concentrations and temperatures were used.

Study	$[Br^-]_{aq}$ / M	$[Cl^-]_{aq}/[Br^-]_{aq}$	$[H^+]_{aq}$ / M	T / °C	Calculated k_r^{Br-}
Disselkamp et al.[110]	$3.9 \cdot 10^{-3}$	510	$3.2 \cdot 10^{-4}$	17	4.7
Oldridge and Abbatt [31]	$8.6 \cdot 10^{-3}$	65	$1.0 \cdot 10^{-2}$	0	4.2
Disselkamp et al.[110]	$1.2 \cdot 10^{-2}$	170	$3.2 \cdot 10^{-4}$	17	6.2
Artiglia et al.[3]	$1.2 \cdot 10^{-1}$	0.8	$1.0 \cdot 10^{-1}$	0	3.5

Table 5. Summary of parameters to model ozone uptake by the surface reaction of O_3 with Br^- in the presence of Cl^- (equation 23).
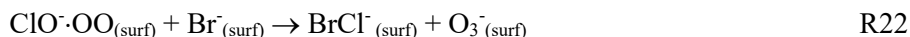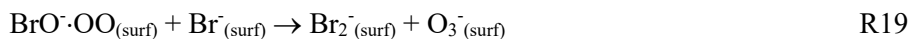
Parameter	Value	Estimated error or range
$E_{a,r}^{Br-}$ / kJ mol^{-1}	14	±10
$k_{r,0}^{Br-}$	$2.1 \cdot 10^3$	$(2 \cdot 10^2, 2 \cdot 10^4)$
K_{Cl} / M^{-1} a,b	0.4	(0, 1.3)
$[Cl^-]_{surf,max}$ a,c / M	10	(5.5, 53)

aThese parameters describe the estimated ratio $[Cl^-]_{surf}/[Cl^-]_{aq}$ for $Na^+/K^+/Cl^-/Br^-$ solutions or particles.
bThe uncertainty range of this parameter has been estimated to be the same as that of Br^- because of lack of more accurate data.
cThe lower limit of this parameter has been estimated as the surficial concentration of $Cl^-_{(surf)}$ reported by Piatkowski et al.[48] The upper limit has been estimated as the maximum geometric capacity considering the radius of chloride is its first hydration shell (0.31 nm).[105]

The following reaction pathway explain the role of Cl^- in the surface reaction of ozone with bromide:

$$O_{3(gs)} + Br^-_{(surf)} \leftrightarrow Br^- \cdot OOO_{(surf)} \qquad\qquad R17$$

$$Br^- \cdot OOO_{(surf)} \leftrightarrow BrO^- \cdot OO_{(surf)} \qquad\qquad R18 \text{ (limiting step)}$$

$$BrO^- \cdot OO_{(surf)} + Br^-_{(surf)} \rightarrow Br_2^-{}_{(surf)} + O_3^-{}_{(surf)} \qquad\qquad R19$$

$$O_{3(gs)} + Cl^-_{(surf)} \leftrightarrow Cl^- \cdot OOO_{(surf)} \qquad\qquad R20$$

$$Cl^- \cdot OOO_{(surf)} \leftrightarrow ClO^- \cdot OO_{(surf)} \qquad\qquad R21 \text{ (limiting step)}$$

$$ClO^- \cdot OO_{(surf)} + Br^-_{(surf)} \rightarrow BrCl^-{}_{(surf)} + O_3^-{}_{(surf)} \qquad\qquad R22$$

However, reaction R17 cannot be limiting because this is a surface accommodation process, which is usually non-limiting (see section 2.1.1). Therefore, we speculate that the adsorbed species, which are likely $Br^- \cdot OOO$ and $Cl^- \cdot OOO$,[3] may undergo an additional chemical transformation that is limiting.

According to theoretical predictions,[3] the product of the transformation of Br·OOO is BrO⁻·OO, and analogously, the transformed chlorine complex may be ClO⁻·OO. The species ClO⁻·OO could then react with Br⁻ forming BrCl⁻, in agreement with the formation of Br_2^- proposed to occur in the surface reaction of ozone with Br⁻.[63] Finally, radical BrCl⁻ may react with itself, forming Br_2.[123]

According to this scheme, Cl⁻ acts as a catalyst in the surface reaction of ozone with Br⁻. According to the scheme proposed above, parameter $k_r^{Br^-}$ is expected to be equal to the rate of reaction R23 relative to the rate of reaction R21. The determined values of $k_r^{Br^-}$ (4-6) imply that the oxidation Cl⁻·OOO→ClO⁻·OO is faster than the analogous oxidation of the brominated species. As this seems unlikely because Br⁻ is usually oxidized faster than Cl⁻, this may suggest that the scheme has not been fully elucidated. Further theoretical and experimental studies are required to clarify the exact mechanism.

The enhancement of the surface reaction Br⁻+O_3 produced by the presence of Cl⁻ is very relevant for both seawater and sea-salt aerosols, which have Cl⁻/Br⁻ ratios of about 650.[124] Therefore, the importance of this pathway will be evaluated as a source of atmospheric bromine in section 2.2.

2.1.3. Study of the influence of H⁺ and other factors on the surface reaction

In this section, the influence of H⁺ on the surface reaction of ozone with Br⁻ will be studied, as well as the influence of low Br⁻ concentrations.

Using PES, Ottoson et al.[125] found that the surface concentration of I⁻ on an iodide salt solution increased by 13% in the presence of HI for a H⁺/I⁻ ratio of 0.2. By analogy, H⁺ may also increase the surficial concentrations of Br⁻ and Cl⁻. Such effect would lead to a higher ozone uptake by the surface reaction O_3+Br⁻. In addition, the presence of H⁺ could also increase uptake through the hypothetical reaction of BrOOO⁻ with H⁺ (R12). Therefore, these two possibilities will be evaluated.

Artiglia et al.[3] determined uptake coefficients using 0.12 M NaBr films at pH=6 (see Figure 2) and at pH 2 using 0.01 M HCl. The "only Br⁻ model", which is only strictly valid for pH=6, estimates the results obtained at pH=2 with a slight error (0.1 %) (see Figure S3). This error is small and could be due to model and experimental inaccuracies. The concentration ratios Cl⁻/Br⁻ and H⁺/Br⁻ for the experiments done at pH=2 are 0.1, so no strong effect of these ions on the surficial concentration of Br⁻ is expected (e.g. Ottoson et al.[118]). Nonetheless, the pH difference between both experiments is large, so if the hypothetical reaction R12 took place, the error obtained should have been positive. In addition, the uptake coefficients determined for a solution containing 0.12-0.24 M NaBr and 0.1 M HCl (pH 1) can be adequately described using the "Br⁻ and Cl⁻ model", which does not take into account the influence of pH (see section 2.1.5). Therefore, reaction R12 is concluded not to take place.

Sakamoto et al.[46] measured gaseous Br_2 formed by the interaction of O_3 with 5-25 mM NaBr at pH 2 using H_2SO_4 at 22 °C for $[O_3]_{gs}$=0.75-3.8 ppm. They determined the Br_2 emission coefficient (ε_{Br2}), which is defined as the rate of gaseous Br_2 release divided by the collision rate of O_3 with the aqueous surface.[46] Considering the solubilities of HOBr and Br_2 and the equilibrium between these species (A1), the uptake coefficient can be up to $1.5\varepsilon_{Br2}$. Figure 6 shows the lower limit of this range ($\gamma^{Br^-}_{lower\ limit}=\varepsilon_{Br2}$) obtained by Sakamoto et al.[46] for $[O_3]_{gs}$=3.8 ppm, as well as the estimated upper limit ($\gamma^{Br^-}_{upper\ limit}=1.5\varepsilon_{Br2}$) as well as the uptake coefficients estimated by several models: the aqueous-phase reaction model, the "only Br⁻ model", and an optimum fit which assumes that the surface reaction rate is 14 times higher than for the "only Br⁻ model".

The underestimation of the uptake coefficients by the "only Br⁻ model" for the conditions used by Sakamoto et al.[46] may be attributed to different factors. First, the present estimation of the surface reaction rate constant ($k_s^{Br^-}$) at ambient temperature may not be accurate, but its estimated uncertainty alone cannot explain the discrepancy. Second, the relatively high H⁺/Br⁻ ratios (0.3-1.6) might lead to

an increase in the surficial concentration of Br⁻. Although the H^+/Br⁻ ratios seem too low to cause a high surface reaction enhancement, the corresponding H^+/Br⁻ ratios at the surface could be higher, as H^+ may be enhanced at the surface relative to the aqueous phase.[126] The fact that SO_4^{2-} has no surface propensity[127] may also favor a surficial enhancement of Br⁻, as otherwise SO_4^{2-} could repel Br⁻ from the surface. Third, H^+ may react with surficial [OOOBr]⁻ (R12), as discussed above. Finally, the [Br⁻]$_{surf}$/[Br⁻]$_{aq}$ ratio could be >5 times higher for the concentrations used by Sakamoto et al.[46] than for the concentration used by Artiglia et al.[3] However, this would imply an extremely high Langmuir equilibrium constant (>100 M⁻¹) that would strongly contrast with the value determined by Wren (<1.3 M⁻¹)[36] for 0.5-6 M Br⁻.

Finally, the underestimation indicated above could suggest that the reaction scheme proposed does not work for some halide concentrations. At low total halide concentrations, O₃ adsorption onto H₂O molecules ("O₃--H₂O sites") may compete with O₃ adsorption onto halide ions ("O₃--Y⁻ sites") (where Y=Cl, Br, or I) because the number of the former is higher. According to a two-site Langmuir model, the percentage of O₃ adsorbed on Y⁻ ions is lower for the Br⁻ concentrations used by Sakamoto et al.[46] than for the higher Y⁻ concentrations used by most other studies analyzed above by up to 35 times (see section S.4.3 in the Supplementary Information). This implies that, if O₃ adsorption on H₂O sites leads to a secondary reaction pathway, the contribution of such pathway could be important at low halide concentrations. However, *i)* this hypothetical reaction pathway is expected to be slower than the main surface reaction, as O₃ adsorbed on H₂O has to translate across the surface to react with a Br⁻ ion; *ii)* at sufficiently low halide concentrations, the aqueous-phase reaction dominates, so the secondary surface reaction would only be important within a limited range of Br⁻ concentrations; *iii)* this secondary pathway is not expected to be relevant in seawater and sea-salt aerosol, where Cl⁻ concentration is high.

Sakamoto et al.[46] obtained, using [Br⁻]$_{aq}$=0.015 M, bromine emission coefficients (ε_{Br2}) which were constant with ozone concentration for the range 0.75-3.8 ppm within experimental error ($\pm 2.5\cdot 10^{-8}$). This error i the maximum possible difference in γ ($\Delta\gamma=1.5\Delta\varepsilon_{Br2}=\pm 3.7\cdot 10^{-8}$) within the studied ozone range, and such small value of $\Delta\gamma$ suggests that the contribution of the surface reaction to uptake is small under Sakamoto et al.'s conditions[34] (see equations 8 and 14). However, the contribution of the surface reaction for the optimum model shown in Figure 6 is 5 times higher, suggesting that the dependence of the surface reaction rate on $O_{3(gs)}$ is not adequately described using a simple Langmuir model. In turn, this supports that O₃ adsorption on O₃--H₂O sites may lead to reaction with Br⁻.
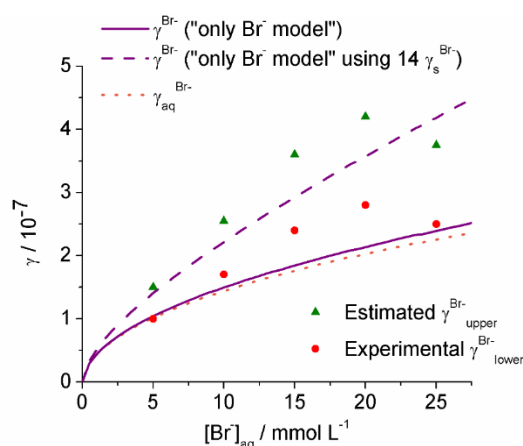

Figure 6. Uptake coefficients for the interaction of ozone (3.8 ppm) with a thin aqueous film containing different concentrations of NaBr and 5·10⁻³ M H₂SO₄ at 22 °C: experimental lower limit of uptake coefficients obtained by Sakamoto et al.[46] (triangles), estimated upper limit of experimental uptake coefficients (squares), and values estimated by the aqueous-phase reaction model, by the "only Br⁻ model", and by a model assuming a the surface reaction rate is 14 times higher than for the "only Br⁻ model" (lines).

2.1.4. Analysis of results from other studies

Liu et al.[58] and other authors[47, 56, 85, 128, 129] have determined the kinetic rate constant of the aqueous-phase reaction of O_3 with Br^-. According to the present model, the aqueous-phase reaction is dominant under their conditions of high O_3 concentration due to surface saturation in ozone. For example, for the concentrations used by Liu et al.[58] (≤0.1 M Br^- and 300 ppm O_3), the surface reaction is predicted to contribute <0.1% of the total uptake. Furthermore, the presence of ClO_4^-, which was added to increase the ionic strength up to 0.1 M, is expected to decrease the contribution of the surface reaction because this large ion displaces Br^- from the surface.[119, 130] These results contribute to support the model.

2.1.5. Summary of the interaction of ozone with Br^- solutions and particles

Figure 7 shows estimated O_3 uptake by pure NaBr solutions and by NaBr/NaCl for different O_3 concentrations for 21 °C and pH 7. According to this figure, for pure NaBr solutions, the uptake by the surface reaction becomes equal to the uptake by the aqueous-phase reaction at $[Br^-]_{aq}>0.1$ M for low O_3 concentrations, such as 0.03 ppm. For mixed NaBr/NaCl solutions containing $[Cl^-]_{aq}=0.5$ M, the surface reaction is dominant for $[Br^-]_{aq}< 0.8$ M. However, the model for mixed NaBr/NaCl solutions (equation 23) has not been evaluated for $[Br^-]_{aq}<3\cdot10^{-3}$ M, and therefore it might not be valid for the lowest Br^- concentrations shown in Figure 7.

The Supplementary Information (section S.4.4) shows a graphic compilation of all results that have not been shown in the present manuscript as estimated by the final models and their comparison to the results by previous studies. Overall, the model fit is good despite the wide range of conditions used.
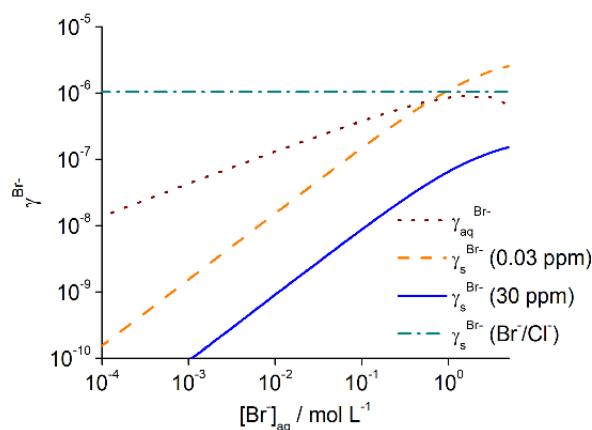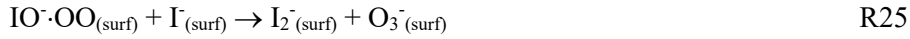

Figure 7. Ozone uptake by the aqueous-phase (γ_{aq}^{Br-}) and the surface reaction (γ_s^{Br-}) of ozone with Br^- in/on NaBr solutions for different gaseous ozone concentrations (0.03 and 30 ppm) as estimated by the "only Br^- model", and ozone uptake by the uncatalyzed and Cl^--catalyzed surface reactions of ozone with Br^- (γ_s^{Br-}) on mixed NaBr/NaCl solutions for $[Cl^-]_{aq}=0.5$ M and $[O_3]_{gs}=0.03$ ppm as estimated "mixed Br^-/Cl^- model" for 21 °C and pH 7.

2.2 Analysis of previous studies of the interaction of O_3 with I^- solutions or aqueous particles

The main unknown variable parameters in the interaction of O_3 with I^- solutions and aqueous particles are all related to the surface reaction: the surface reaction rate constant (k_s^{I-}), the parameters that describe the surficial concentration of iodide ($[I^-]_{surf}$) as a function of $[I^-]_{aq}$ (see equation 15), the adsorption

equilibrium constant of ozone (K_{O3}^{I-}), and the value of parameter p^{I-}, which affects the surface accommodation coefficient ($\alpha_{s,I-}$). It will be initially be assumed that the partial order of $I^-_{(surf)}$ for the surface reaction $I^- + O_3$ is 0 ($z=0$ in equation 14), since this reaction is expected to follow an analogous scheme as the one inferred for $Br^-_{(surf)} + O_{3(int)}$:

$$O_{3(gs)} + I^-_{(surf)} \leftrightarrow I^- \cdot OOO_{(surf)} \qquad \text{R23}$$

$$I^- \cdot OOO_{(surf)} \leftrightarrow IO^- \cdot OO_{(surf)} \qquad \text{R24 (limiting)}$$

$$IO^- \cdot OO_{(surf)} + I^-_{(surf)} \rightarrow I_2^-{}_{(surf)} + O_3^-{}_{(surf)} \qquad \text{R25}$$

Sakamoto et al.[34] determined the apparent uptake coefficients and the number of I_2 molecules emitted to the gas phase for a $5 \cdot 10^{-3}$ M NaI solution exposed to different concentrations of $O_{3(g)}$ for 0.7 s at room temperature, which will assumed to be 21 °C. The real uptake coefficients were not reported in the study by Sakamoto et al.[34], but they can be obtained from the apparent uptake coefficients and their measurements of gaseous iodine using two equations that will be indicated next:[40]

$$\frac{[O_3]_{gs}}{[O_3]_g} = \frac{K_{O3,eff}^{I-}}{K_{O3}^{I-}} \qquad (24)$$

where $K_{O3,eff}^{I-}$ is the apparent equilibrium constant of ozone, which has been determined[40] to be $3.6 \cdot 10^{-15}$ cm^3 molecule^{-1} under the conditions used by Sakamoto et al. The second equation is the following one:[131]

$$\frac{[O_3]_{gs}}{[O_3]_g} = \frac{\gamma_{eff}^{I-}}{\gamma^{I-}} \qquad (25)$$

Apart from the results by Sakamoto et al.[34], another result must be used to constrain the values of the unknown parameters and variables. This result will be drawn from the study by Rouviere et al.[106], who obtained an uptake coefficient of $1.2 \cdot 10^{-2}$ for 7 M KI aerosols using $[O_3]_{gs}=0.07-0.17$ ppm. Considering the low O_3 solubility, the activity coefficient of I^-, and the higher I^- concentrations that are present in the narrow reacto-diffusive region that is formed under their conditions[48], we estimate an approximate uptake by the aqueous-phase reaction of only about $1 \cdot 10^{-3}$ with the present model (equation 8). Therefore, we attribute ozone consumption mostly to the surface reaction under their conditions. A similar argument can be given for other studies[67, 112] done at high I^- concentrations. [64, 106 64, 106 64, 106 67, 111 68, 112 67, 111] However, this conclusion is quite uncertain, as all of these studies obtained similar uptake coefficients ($1.1 \cdot 10^{-2}$-$1.5 \cdot 10^{-2}$), suggesting the aqueous-phase reaction dominates. For the uptake coefficient obtained by Rouviere et al.[106] for $[I^-]_{aq}=7$ M, it will be assumed that $[I^-]_{surf}=11$ M, which is close to the value determined by Piatkowski et al.[48] for $[I^-]_{aq}=3$ M.

The concentration ratio $[I^-]_{surf}/[I^-]_{aq}$ for $[I^-]_{aq}=5 \cdot 10^{-3}$ M and the parameters K_{O3}^{I-}, k_s^{I-}, p^{I-} can be determined by assuming initial values for them and modifying them iteratively until the minimum model error is reached with respect to the Sakamoto et al.'s coefficients and O_3 concentrations (their Figure 5A)[34]. In addition, the equality drawn from Rouviere et al.[106] must be met. However, infinite mathematical solutions are possible. All the solutions yield surface to aqueous-phase concentration ratios ($[I^-]_{surf}/[I^-]_{aq}$) higher than 300 for $[I^-]_{aq}=5 \cdot 10^{-3}$ M. However, this seems to disagree with an ESI-MS study[119] where it was found that $[I^-]_{surf}$ is about 3 times higher than $[Br^-]_{surf}$ for a solution containing micromolar amounts of these ions. According to the present model, $[Br^-]_{surf}/[Br^-]_{aq}$ is 6 at low Br^- concentrations and, therefore, $[I^-]_{surf}/[I^-]_{aq}$ is estimated ~20, which is much lower than the ratio $[I^-]_{surf}/[I^-]_{aq}>300$ inferred above. Furthermore, the ratio $[I^-]_{surf}/[I^-]_{aq}>300$ inferred above would imply a Langmuir constant K_I of 33 M^{-1}, which is higher than the value of 23 M^{-1} determined by Reeser et al.[35] under conditions of gas-phase resistance. As the source of these discrepancies is unknown, the logarithmic mean between 20 and 300 (80) will be assumed for the ratio $[I^-]_{surf}/[I^-]_{aq}$ at low I^- concentrations.

The final parameters for the surface reaction of O_3 with I^- in pure KI/NaI aqueous media are summarized in Table 6. This model will be referred as "only I^- model". The values of K_I and $[I^-]_{surf,max}$ for equation 15 have been determined using the ratio of $[I^-]_{surf}/[I^-]_{aq}$ estimated in the present work and the one determined by Piatkowski et al.[48]

Despite the high uncertainty in $[X^-]_{surf}/[X^-]_{aq}$, this uncertainty does not influence the uptake much at low X^- concentrations because it is compensated by the error in $k_s^{X^-}$. However, the uncertainty is influential at high X^- concentrations (about $[Br^-]_{aq}>1$ M and $[I^-]_{aq}>0.05$ M). The present model for the ozone interaction with I^- solutions/particles overestimates the uptake coefficient at high I^- concentrations. For $[I^-]_{aq}=7$ M and $[O_3]_{gs}=0.07$-0.15 ppm, the model estimates a uptake coefficient of 0.06, whereas the uptake measured[106] is 0.01 (with one significant figure). Activity coefficients of surficial ions could be the source of the discrepancy, as they are expected to be different from 1 at such high concentrations.

Figure 8 shows the uptake coefficients estimated by this model along with the uptake coefficients estimated from the experimental results by Sakamoto et al.[34] The determined value of $K_{O3}^{I^-,21\ °C}$ for an iodide-containing aqueous surface ($2.1\cdot10^{-14}$ cm^3 molecule^{-1}) is close to the estimated value of $K_{O3}^{Br^-,21°C}$ for bromide ($2.0\cdot10^{-14}$ cm^3 molecule^{-1}), supporting the model. This could suggest that the energy of adsorption between ozone and an ionic substrate is not highly specific to the nature of the ion but mainly depends on the charge of the ion. However, determinations of K_{O3}^{subs} for other ions are needed to reach definite conclusions about this subject. Using the determined values of $K_{O3}^{Br^-,0°C}$ and $K_{O3}^{I^-,21°C}$, an empirical function $K_{O3}^{X^-}(T)$ can be obtained for both halides, defined by equation 16 and the parameters $C=7.2\cdot10^{-26}$ cm^3 molecule^{-1} and $\Delta H_{ads}=65$ kJ mol^{-1}.
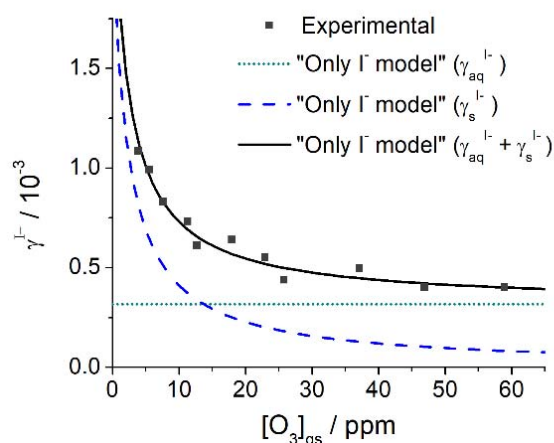

Figure 8. Uptake coefficients for the interaction of O_3 with a $5\cdot10^{-3}$ M NaI solution as a function of $O_{3(gs)}$ concentration: values derived from experimental data by Sakamoto et al.[34] (squares) and values estimated by the "only I^- model" estimated for the aqueous-phase reaction, surface reaction, and both reactions, of ozone with I^- (lines).

As explained in the Model Description section, it has been assumed that the surface reaction and the aqueous-phase reaction of ozone with iodide are parallel, which may not be the case at high I^- concentration, for which uptake is high. However, if the model which does not assume parallel reactions is used (see section S.1), very similar uptake coefficients are obtained. However, the coefficients cannot be refined using this more complex model because its parameters are uncertain.

The rate constant determined in the present work for the surface reaction I^-+O_3 is about 10^4 higher than the rate constant of the surface reaction Br^-+O_3. This compares with a ratio of about 10^7 for the aqueous-phase reactions at the same temperature. However, the order of the surface reactions is first, while that of the aqueous-phase reactions is second.

Table 7 summarizes the evaluated parameters of the aqueous-phase reaction I^-+O_3. The rate constant of this reaction in pure KI/NaI solution at room temperature has not only been investigated by Liu et al.[58] ($1.2 \cdot 10^9$ M^{-1} s^{-1}) but also by Shaw and Carpenter[75], who used lower I^- and O_3 concentrations, and obtained a similar value ($1.4 \cdot 10^9$ M^{-1} s^{-1}). The small difference among both values suggests a small surface contribution in the latter study[75]. The present model agrees well with this inference, as it estimates a surface reaction contribution of 18-24% under their conditions and explains the higher "apparent" aqueous-phase rate constant determined in their work[75]. In addition, the approximate agreement of the present model with their results supports the assumed partial order of $I^-_{(surf)}$ because Shaw and Carpenter[75] employed I^- concentrations several orders of magnitude different from Sakamoto et al.[34].

According to the scheme proposed for Br^-, the chloride ion is expected to be involved in the surface reaction of ozone with I^-. Analogously to proposed reaction R24 for bromine species, the following reaction is expected to occur if reaction R24 is correct:

$$ClO^-\cdot OO_{(surf)} + I^-_{(surf)} \leftrightarrow ICl^-_{(surf)} + O_3^-{}_{(surf)} \qquad \text{R26}$$

Assuming R23 and R27 are limiting and R29 is not, the kinetic equation for the surface reaction of O_3 with I^- in I^-/Cl^- solutions or particles is as follows:

$$\gamma_s^{I^-} = \frac{4k_s^{I^-}}{\omega} \frac{K_{O_3}^{I^-}}{(1+K_{O_3}^{I^-}[O_3]_{gs})} \left(\frac{K_I[I^-]_{aq}[I^-]_{surf,max}}{1+K_I[I^-]_{aq}} + k_r^{I^-} \frac{K_{Cl}[Cl^-]_{aq}[Cl^-]_{surf,max}}{1+K_{Cl}[Cl^-]_{aq}} \right) \qquad (27)$$

where $k_r^{I^-}$ is equal to $k_s^{Br-}\cdot k_r^{Br-}/k_s^{I^-}$. The model where $\gamma_s^{I^-}$ is described by equation 27 will be referred as "mixed I^-/Cl^- model" (see Table 6 for its parameters). The constant $k_s^{I^-}$ is about 10^5 times than k_s^{Br-} and the rate constant of the proposed reaction R23 ($k_s^{Br-}\cdot k_r^{Br-}$). According to this scheme, I^- oxidation by O_3 through formation of $ClO^-\cdot OO_{(surf)}$ (R23) is significant in comparison to I^- oxidation through formation of $IO^-\cdot OO_{(surf)}$ (R27) when Cl^-/I^- ratios are about >1000, such as those that may be found in seawater and aerosol.

The hypothesis that Cl^- catalyzes the surface reaction of ozone with I^- may seem to disagree with previous comparisons of iodine emissions in solutions exposed to ozone.[1, 47] These emissions were about twice higher for pure NaI/KI solutions than for seawater solutions containing the same I^- concentration. [1, 47] If Cl^- has a positive influence on the surface reaction of ozone with I^-, seawater solutions could be expected to emit more iodine than pure NaI/KI solutions containing the same I^- concentration. The difference in iodine emissions has been attributed to the role of organic surfactants in seawater as a physical barrier to mass volatilization.[75] Therefore, the possibility that Cl^- catalyzes the surface reaction of I^-+O_3 cannot be discarded, as the blocking effect of organics could mask this influence if only iodine emissions are studied. In fact, Garland et al.[47] evaluated the rate constant of the aqueous-phase reaction I^-+O_3 by measuring O_3 consumption by iodide-spiked seawater, and obtained a value that is about twice higher than the one obtained by Liu et al.[58] As evaluated in the next section, this supports the hypothesis that Cl^- catalyzes the surface reaction I^-+O_3.

Except for seawater, there have only been a few studies of the interaction of ozone with mixed I^-/Cl^- solutions or aqueous particles. Rouviere et al.[106] studied the interaction of ozone with KI/NaCl aerosols and they found no significant effect of Cl^- on the reactivity, but they used low Cl^-/I^- ratios for which the "I^- and Cl^- model" estimates that Cl^- has no effect. Enami et al.[70] studied this interaction using aqueous mixed I^-/Br^-/Cl^- microparticles, and detected surficial ICl_2^- and IBr_2^-, which may be formed through several equilibrium reactions from Table 1. Carpenter et al.[1] reported that I_2 emissions by I^- solutions increased in the presence of Cl^-, which they attributed also to reactions in Table 1. However, the catalytic effect proposed in this work is also expected to intervene under their conditions.

Figure 9a shows the separate contributions to ozone uptake by the aqueous-phase reaction and by the surface reaction for pure NaI solutions and mixed NaI/NaCl solutions for different concentrations.

Figure 9b shows the percentage that the surface reactions contribute to the total uptake for the same conditions. As seen in this figure, the uptake coefficients by each reaction in pure NaI solutions become equal within the I$^-$ concentration range 10^{-4}-10^{-2} M for the O$_3$ concentrations shown. The model for mixed NaI/NaCl solutions (equation 23) has not been evaluated for $[I^-]_{aq}<10^{-7}$ M, and therefore these concentrations are not shown in Figure 9. For the typical I$^-$ concentration of $1\cdot10^{-7}$ M that is present in surface seawater[77] and a typical O$_3$ concentration in the remote troposphere (0.03 ppm),[8] the estimated contribution is only 35%. However, the effect of seawater media must be evaluated to estimate the ozone uptake by seawater I$^-$ (see next section).

Just as Cl$^-$ catalyzes the oxidation of I$^-$ and Br$^-$ by O$_3$, it is plausible that the oxidation of I$^-$ by O$_3$ is also catalyzed by Br$^-$ according to the following reaction that is analogous to reaction R24 and R29:

$$BrO^-\cdot OO_{(surf)} + I^-_{(surf)} \rightarrow IBr^-_{(surf)} + O_3^-_{(surf)} \qquad\qquad R30$$

If this hypothesis is correct, then the generation of volatile bromine products following ozone uptake by seawater is inhibited to some extent by I$^-$ and the generation of volatile iodine products from ozone uptake is enhanced by Br$^-$. However, the extent by which this may happen needs to analyzed by obtaining data of ozone uptake by mixed I$^-$/Br$^-$ solutions. Considering [I$^-$]/[Br$^-$] ratios are low in seawater (1/8000), the extent of reaction R30 could be minor compared to R25 and will not be considered in the present work.
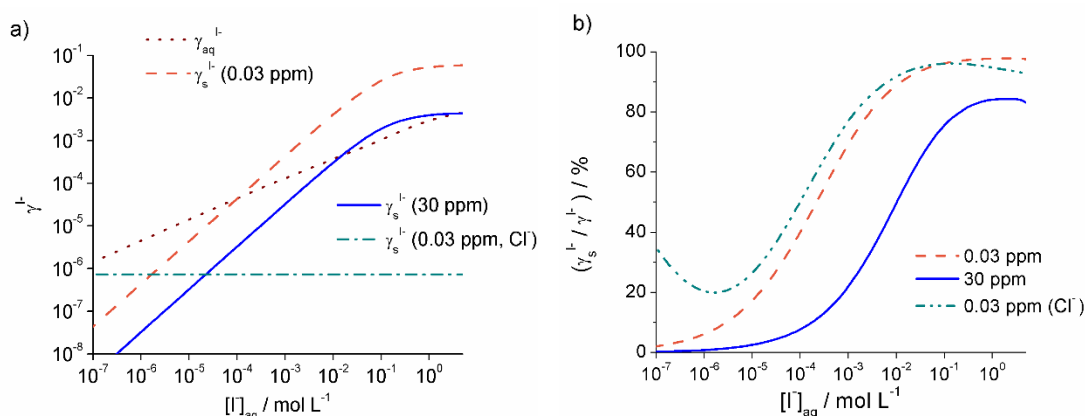

Figure 9. Ozone uptake by the aqueous-phase ($\gamma_{aq}^{I^-}$) and surface ($\gamma_s^{I^-}$) reaction of ozone with I$^-$ in/on pure NaI solutions as estimated by the "only I$^-$ model" and ozone uptake by the Cl$^-$-catalyzed surface reactions of ozone with I$^-$ on mixed NaI/NaCl solutions containing $[Cl^-]_{aq}$=0.55 M as estimated by the "mixed I$^-$/Cl$^-$ model" (a). Contribution (%) of the surface reaction O$_3$+I$^-$ to total ozone uptake by pure NaI solutions as estimated by the "only I$^-$ model", and contribution (%) of both the uncatalyzed and Cl$^-$-catalyzed surface reactions I$^-$+O$_3$ to total uptake by mixed NaI/NaCl solutions containing $[Cl^-]_{aq}$=0.55 M as estimated by the "mixed I$^-$/Cl$^-$ model" (b). Different ozone concentrations (0.03 and 3 ppm) have been plotted at 21 °C and pH=7.

Table 6. Summary of parameters to model ozone uptake by the surface reaction of O$_3$ with I$^-$ in pure NaI/KI solutions or aqueous particles ("only I$^-$ model" and equation 14, where z=0) and in mixed I$^-$/Cl$^-$ solutions and aqueous particles ("mixed I$^-$/Cl$^-$ model" and equation 27).

Parameter	Value	Estimated error or range
$k_s^{21\,°C}$ / s^{-1} [a]	140	(20, 2000)
K_I / M^{-1} [b,c]	7.3	(0.4, 23)
$[I^-]_{surf,max}$ / M [b,d]	11.0	(10.5, 36)
$K_{O3}^{I-,21\,°C}$ / 10^{-14} cm^3 molecule^{-1}	2.1	±0.2
p^{I-} / 10^{-15} cm^2 molecule^{-1}	1.3	(0.5, 1.3)

$k_r^{I-,21\,°C}/10^{-4}$ [e]	3.5	(0.35, 35)

[a] This rate constant was estimated using results by Sakamoto et al.[34], who did not report the exact room temperature at which their experiments were done.

[b] The value of these parameters, which describe the ratio $[I^-]_{surf}/[I^-]_{aq}$ in pure NaBr/KBr solutions, are very uncertain. In addition, they may change in the presence of other species (see discussion throughout the present work).

[c] The lower limit of this parameter is estimated to be the value of K_{Br} determined in the present work, while the upper limit is estimated as a value of K_I that has been determined[35] in the presence of gas-phase resistance.

[d] The lower limit of this parameter has been estimated as equal to the only reported surficial concentration of iodide, which is 10.5 M (for 3 M)[48]. The upper limit has been estimated as the geometric maximum using the radius of iodide[105].

[e] This value has not been determined using kinetic results of the reaction I^-+O_3, but it instead has been inferred to be $k_s^{Br-}·k_r^{Br-}/k_s^{I-}$ (see text). However, kinetic results obtained using iodide-spiked in seawater support its validity (see section 2.3).

Table 7. Summary of evaluated parameters to model ozone uptake by the aqueous-phase reaction of O_3 with I^- (equation 8).

Parameter	Value	Reference
Rate constant at 25 °C (k^{I-})	$1.2·10^9\,M^{-1}\,s^{-1}$	Liu et al.[58]
Activation energy of the reaction (E_a^{I-})	~0 kJ mol^{-1}	MacDonald et al.[77]

2.3 Ozone uptake by seawater and sea-salt aerosol Br$^-$ and I$^-$

In this section, ozone uptake by reaction with I^- and Br^- in/on surface seawater and sea-salt aerosol (SSA) at 21 °C and/or 3 °C will be estimated. In order to do so, it is first necessary to evaluate the effect of compounds present in these media on the parameters that influence the uptake.

2.3.1 Parameters and variables required to model uptake by seawater and sea-salt Br$^-$ and I$^-$

The aqueous-phase reaction parameters that are different in seawater and SSA with respect to pure $Na^+/K^+/I^-/Br^-/Cl^-$ solutions are the ozone solubility (s), the aqueous-phase diffusivity of ozone (D_{aq}), and the activity coefficients (γ_{X-}), and the reacto-diffusive length (l^{X-}). The surface reaction parameters that are expected to change in the presence of other species are the adsorption equilibrium constant of the reacting halide X^- (K_X) and/or the maximum concentration of X^- at the surface ($[X^-]_{surf,max}$).

Activity coefficients of Br^- and I^- and aqueous-phase diffusivities of ozone will be calculated considering only the presence of the major salt, NaCl (see Model Description section). The concentration of NaCl in seawater is about 0.55 M, while it is estimated to be about 5 M in SSA.[28, 45, 132] For these concentrations, the activity coefficients of Br^- and I^- are estimated as 0.8 and 3 in seawater and sea-salt aerosol, respectively.

The presence of organics in seawater and sea-salt aerosol may increase the ozone solubility[108, 112] and decrease the ozone diffusivity through an increase of aqueous-phase viscosity[13, 52, 53] with respect to inorganic solutions.[52, 55,114, 134, 135] The effect on the solubility could be moderate, as suggested by different studies[108, 112] where solutions containing Br^- and/or citric acid were exposed to ozone, but it is not clear whether the net effect is negative[112] or positive[108]. By contrast, the effect of organics on viscosity, and therefore on the diffusivity of aqueous molecules,[80] may be strong if the organic content is high. For example, secondary organic aerosol[133] and solutions containing a high concentration of organics[134] may have viscosities several orders of magnitude higher than water. By contrast, the viscosity of a solution containing 0.3 M NaBr and 0.3 M citric acid was only 30% higher than the viscosity of pure water.[112] For simplicity, the ozone solubility and diffusivity in seawater and SSA will

be assumed to be determined by its NaCl content for simplicity (see section S.2.1 in the Supplementary Information). The estimated O_3 solubilities in seawater and SSA are 14% and 72% lower than the solubility in pure water, respectively. The estimated aqueous diffusivity values for these systems are 2% and 40% lower, respectively, than for pure water (see section S.2.3).

For media containing more than one reactive solute toward ozone, the reacto-diffusive length is calculated considering the main aqueous-phase reactions that leads to O_3 uptake:

$$l^{X-} = \sqrt{\frac{D_{aq}}{\sum k^i \cdot [i]_{aq}}} \tag{28}$$

where i is each aqueous reactant and k^i is the rate constant of the aqueous-phase reaction of reactant i with ozone. For such multicomponent media, the uptake equation for the aqueous reaction $X^- + O_3$ is obtained by combining equations 8 and 10:

$$\Gamma_{aq}{}^{X-} = \frac{4 \cdot s \cdot k^{X-} \cdot l^{X-} \cdot f \cdot a_{X-}}{\omega} \tag{29}$$

The main contributors to O_3 uptake in seawater are believed to be I^- and dissolved organic matter (DOC).[1, 102, 109, 135, 136] The product $k^{DOC} \cdot [DOC]_{aq}$ in ocean seawater has been reported to be about 100 s^{-1}.[135] In aerosol, the reaction of O_3 with Fe^{2+} in sea-salt aerosol that are internally mixed with dust aerosol may compete to some extent because the rate constant of this reaction is high (about 10^6 M^{-1} s^{-1}).[137, 138] For simplicity, it will be assumed that the main species taking up ozone is iodide for the calculation of l^{X-} in sea-salt aerosol through equation 28.

In order to estimate the rates of the surface reactions of O_3 with I^- and Br^- in seawater and SSA, it is necessary to estimate the surficial concentration of I^- and Br^- in these media. Chloride has been found to increase these concentrations in theoretical and experimental studies.[66, 121] The effects of organics on these concentrations have been studied using X-ray photoelectron spectroscopic (XPS) in several studies.[108, 139, 140] One of them reported that bromide was suppressed at the surface by 30% in the presence of 2.5 M citric acid in a 0.1 M NaBr solution.[108] Similarly, another XPS study[139] found that the I^-/K^+ ratio at the surface of a ~7 M KI solution was repressed by about 50% when a tert-butanol/water mole ratio of 0.06 was used. Recently, Lee et al.[140] found that the presence of butyric acid represses the surficial concentrations of Br^- and I^-,[1, 47] but the presence of 1-butanol increases them. As the net effect produced by Cl^- and organics is difficult to predict with available data, it will be assumed that $[I^-]_{surf}$ and $[Br^-]_{surf}$ in seawater and sea-salt aerosol do not change with respect to pure salt solutions. The concentration $[Cl^-]_{surf}$ will be estimated below.

A value of the rate constant of the aqueous-phase reaction $I^- + O_3$ that was determined[47] using I^--spiked seawater will be used to evaluate the hypothesis that Cl^- catalyzes the surface reaction $I^- + O_3$, as well as to estimate $[Cl^-]_{surf}$ in seawater. This will be done by fitting the uptake coefficients estimated by the "mixed I^-/Cl^- model" for the I^- and O_3 concentrations used by Garland et al.[47] to the correlation $1/\gamma^{I-}$ and $1/a_I{}^{0.5}$ expected for the aqueous-phase reaction (see section S.5 in the Supplementary Information). This correlation leads to an "apparent" rate constant of $3.1 \cdot 10^9$ M^{-1} s^{-1}, which is higher than the actual value ($1.2 \cdot 10^9$ M^{-1} s^{-1}),[58] supporting a catalytic effect by $Cl^-_{(surf)}$. Assuming the difference between this value and the value determined by Garland et al.[47] comes entirely from $[Cl^-]_{surf}$, this variable can be varied to match the value by Garland et al.[47], yielding 0.86 M (as opposed to the prediction of 1.8 M estimated in the present work for pure NaCl solutions). Therefore, $[Cl^-]_{surf}/[Cl^-]_{aq}$ in seawater is estimated to be 1.6, which is the same as the value reported by Piatkowski et al.[48] for $[Cl^-]_{aq} = 3$ M.[48] It will be assumed that $[Cl^-]_{surf}/[Cl^-]_{aq}$ in sea-salt aerosols is also 1.6. However, the assumption that reaction R22 is non-limiting may not be accurate at low I^-/Cl^- ratios. Therefore, the estimation of $[Cl^-]_{surf}$ and the contribution of the surface reactions $X^- + O_3$ in seawater are uncertain.

2.3.2 Estimation of ozone uptake by seawater and sea-salt aerosol Br⁻ and I⁻

Figure 10 shows the estimated contributions of the aqueous-phase reaction, the uncatalyzed surface reaction, and the Cl⁻-catalyzed surface reaction of O_3 with I⁻ to ozone uptake in seawater for the usual range of I⁻ concentrations at 21 °C. As it can be inferred, the contribution of the catalyzed surface reaction can be as large as that of the aqueous-phase reaction at low I⁻ concentrations, but it is significant for all I⁻ concentrations in seawater. The total uptake ranges from $1 \cdot 10^{-6}$ to $2 \cdot 10^{-6}$. These results need to be included in models to estimate ozone uptake by seawater.[1] In order to model iodine emissions, the effect of organics on iodine volatilization[1, 32, 35, 75] and possible reactions of the intermediate [OOOI]⁻ with organics[141] need to be considered as well.
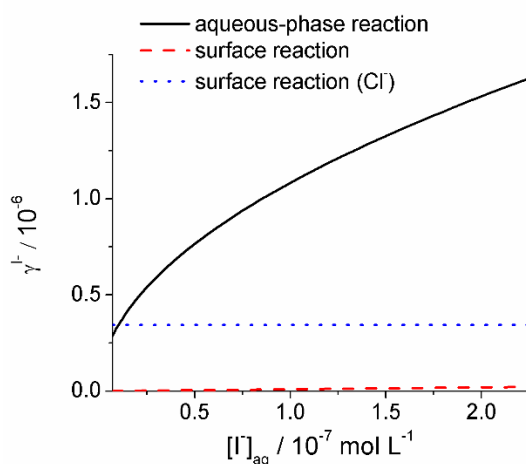

Figure 10. Estimated contributions of the aqueous-phase reaction, the uncatalyzed surface reaction, and the Cl⁻-catalyzed surface reaction of O_3 with I⁻ to ozone uptake by surface seawater at 21 °C. Note: scales are not logarithmic.

According to the present model, the occurrence of the surface reaction I⁻+O_3 is not readily detected by an analysis of the type of correlation between $[I^-]_{aq}$ and measured uptake (γ^{I-}) when the contribution of the surface reaction is only partial. For example, for the conditions used by Shaw and Carpenter[75], the present model-estimated total uptake fits an aqueous-phase reaction correlation ($1/\gamma$ vs. $1/[I^-]_{aq}^{0.5}$) with a regression coefficient of >0.9999, even though the surface contribution is estimated to be 18-24%. In addition, if the correlation between $[O_3]_{gs}$ and uptake is studied for low values of $[O_3]_{gs}$, a surface contribution may not be detected, as in this case the type of relation between $[O_3]_{gs}$ and uptake (constant) is the same as for the aqueous-phase reaction. The surface contribution may not be detected either if the correlation between $[O_3]_{gs}$ and product formation is studied, as in this case the type of relation between $[O_3]_{gs}$ and product emission (proportionality) are the same as for the aqueous-phase equation. The conditions and high O_3 concentrations (650-970 ppm) used by Liu et al.[58] are the most adequate among those used in literature to determine the aqueous-phase reaction rate constant because, according to the present model, the surface reaction makes only a slight contribution (<1%) under these conditions. This evaluation of the most reliable rate constant of the aqueous-phase reaction I⁻+O_3 represents an improvement of our previous work[40].

The estimated ozone uptake by reaction with sea-salt aerosol (SSA) iodide for different size at 21 °C is shown in Figure 11 as a function of I⁻ concentration. The I⁻ concentrations in this figure range from a low concentration of 10^{-8} M (i.e., almost full I⁻ depletion) to the estimated initial concentration in sea-salt aerosol in the absence of I⁻ enhancement over conservative tracer Na⁺ (10^{-6} M) times an enhancement factor of 10, because the I⁻/Na⁺ ratio could increase during the process of sea-salt aerosol generation from seawater.[42, 43, 142] A wide range of concentrations is shown because the iodide concentration in aged aerosol has not been clarified.[6, 141, 143, 144] According to Figure 11, the surface reactions of ozone with iodide can dominate uptake under many conditions. For $[I^-]_{aq} < 10^{-6}$ M, the Cl⁻-

catalyzed surface reaction dominates. For higher concentrations than about 10^{-6} M, either the uncatalyzed surface reaction or the aqueous-phase reaction are estimated to dominate, depending on the aerosol size. Total uptake in fresh aerosol is estimated to be $3 \cdot 10^{-6}$. These conclusions contrast with our estimations in a previous study[40] where the surface reaction rate had not been accurately modeled and the effect of Cl$^-$ on this rate had not been recognized.
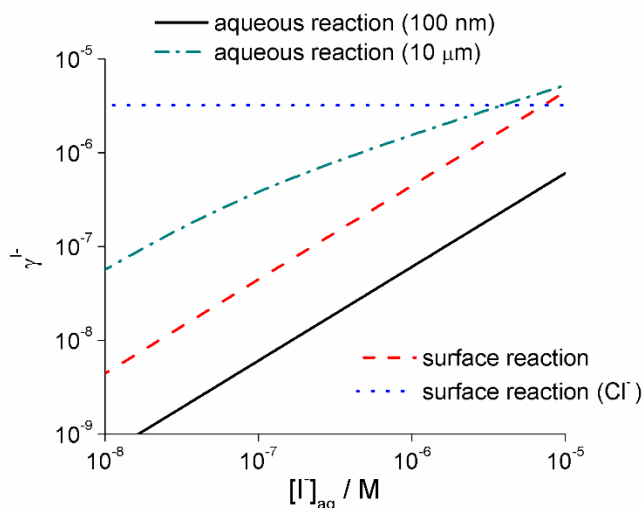

Figure 11. Estimated contributions of the aqueous-phase reaction, uncatalyzed surface reaction, and the Cl$^-$-catalyzed surface reaction of ozone with I$^-$ to ozone uptake by sea-salt aerosol of different diameter at 21 °C assuming $[Cl^-]_{surf} = 1.6[Cl^-]_{aq} = 8.0$ M.

The ozone uptake estimated by the aqueous-phase and surface reactions of ozone with bromide in seawater is shown in Figure 13 as a function of the iodide concentration for $[Br^-]_{aq}=9 \cdot 10^{-4}$ M,[124] $[O_3]_{gs}=0.03$ ppm, and pH=8.2[138, 145] at 21 °C. For comparison, the estimated uptake at 3 °C for the dominant pathway, which is the Cl$^-$-catalyzed surface reaction, is also shown. The uptake coefficient by the catalyzed reaction is $(2-4) \cdot 10^{-7}$ at 3-21 °C, which is only about 5 times lower than ozone uptake by its reactions with seawater I$^-$. Taking this into consideration, the surface reaction with seawater Br$^-$ may represent a significant source of atmospheric bromine. However, in order to model this source accurately, it is necessary to investigate whether the direct reaction product of the surface reaction is HBrO, BrO$^-$, or another product, as seawater pH (8.2) is close to pK$_a$ of HBrO (8.7).
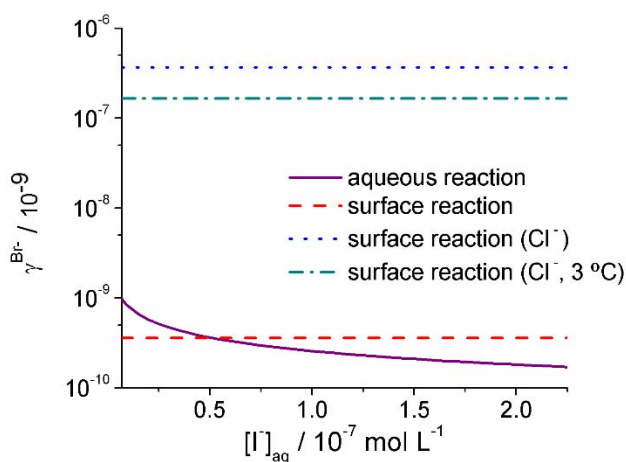

Figure 12. Estimated contributions of the aqueous-phase reaction, uncatalyzed surface reaction, and the Cl$^-$-surface reaction of ozone with Br$^-$ to ozone uptake by seawater for $[Br^-]_{aq}=9 \cdot 10^{-4}$ M and $[O_3]_{gs}=0.03$ ppm as a function of I$^-$ concentration for different temperature (21 °C unless otherwise indicated in the key).

Figure 13 shows the ozone uptake estimated for the aqueous-phase and surface reactions with sea-salt aerosol Br⁻ of different size (100 nm, 10 μm) at 21 °C as a function of I⁻ concentration for different aerosol size assuming $[Br^-]_{aq}=9\cdot10^{-3}$ M and pH 5. This concentration has been chosen because Br⁻ has been determined to have enhancement factors (*EF*) of about 0.6 in marine SSA, except in some fine aerosol.[44, 45] As in seawater, the Cl⁻-catalyzed surface reaction of ozone of bromide dominates uptake, which in this case is $3\cdot10^{-6}$. According to the present model, pH only influences the uptake by the aqueous-phase reaction Br⁻+O₃, whose contribution to uptake is minor, and therefore pH scarcely has any influence on the total uptake in this system.
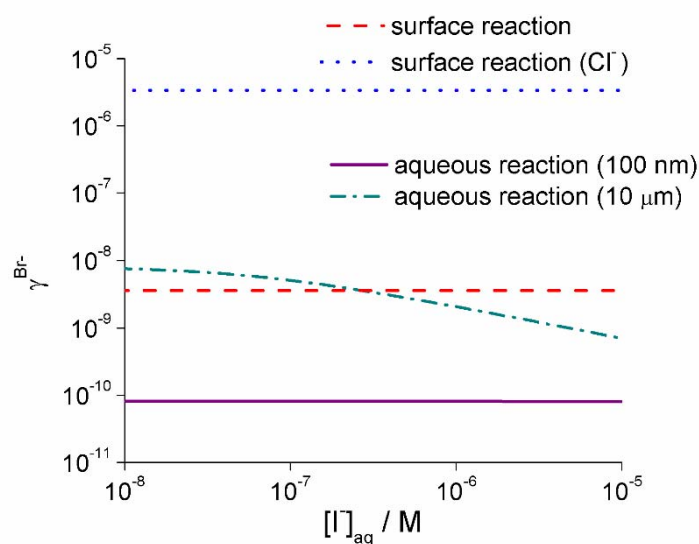

Figure 13. Estimated contributions of the aqueous-phase, uncatalyzed surface reaction, and Cl⁻-catalyzed reaction of ozone with Br⁻ to ozone uptake by sea-salt aerosol for $[Br^-]_{aq}=9\cdot10^{-3}$ M at 21 °C as a function of iodide concentration assuming $[Cl^-]_{surf}=1.6[Cl^-]_{aq}=8.0$ M and pH 5 for different particle diameter shown in the legend.

In order to make more accurate estimations of ozone uptake by seawater and sea-salt aerosol, the total effect of all compounds on the surficial concentration of halides should be studied. Furthermore, it should be studied whether I⁻ competes reacts significantly with [OOOBr]⁻ at the seawater surface, as this would lead to higher iodine emissions and to lower bromine emissions, as discussed in section 2.2. In addition, organics may have several effects on the ozone uptake. First, as indicated above, they increase the viscosity of the aqueous phase,[52, 53] and therefore increase the resistance to diffusion in the aqueous phase, decreasing the ozone uptake.[52, 53, 55, 130, 131, 133-135] Second, many organics accumulate at the surface (e.g. Werner et al.[146]) and may exert resistance to gas exchange.[35, 75] Finally, as proposed recently,[141] certain unsaturated organics may react with the intermediate adduct [OOOI]⁻ in surface reaction where I⁻ acts as a catalyst; therefore, these organics may lower iodine emissions.

Conclusions

The aqueous halides I⁻ and Br⁻ react with O₃ via three reaction pathways: an aqueous-phase reaction, an uncatalyzed Langmuir-Hinshelwood reaction, and a Langmuir-Hinshelwood reaction catalyzed by Cl⁻. The catalyzed reaction is estimated to contribute significantly to inorganic iodine emissions by seawater and sea-salt aerosol, and to dominate inorganic bromine emissions by seawater and sea-salt aerosols. Therefore, this reaction needs to be included in tropospheric models to estimate these emissions.

In future studies, the parameters of the surface reactions should be refined. The parameters related to the surface concentration of the reacting halides are especially uncertain, both for pure halide solutions and for multicomponent solutions. A very high enhancement of the surface concentration of I⁻ relative

to its aqueous-phase concentration (>20) is suggested by this study. The temperature dependence of the surface reactions of ozone with I^- needs to be determined (using $[I^-]_{aq} > 10^{-4}$ M), and that of the surface reactions of ozone with Br^- needs to be refined (using $[Br^-]_{aq} > 0.1$ M). In addition, the catalytic effect of Cl^- and the possible catalytic effect of Br^- on the surface reactions need to be determined with more accuracy. For a NaCl concentration of 0.5 M, the Cl^--catalyzed surface reactions $X^- + O_3$ (X=I, Br) are expected to be significant for a wide range of I^- and, especially, Br^- concentrations. Finally, the products of the reactions should be investigated.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1. L. J. Carpenter, S. M. MacDonald, M. D. Shaw, R. Kumar, R. W. Saunders, R. Parthipan, J. Wilson and J. M. C. Plane, *Nature Geosci.*, 2013, 6, 108-111.
2. S. T. M., E. M. J., S. D. V., C. L. J., C. Rosie, B. A. R., S. J. A. and B. T. J., *Geophysical Research Letters*, 2016, 43, 10012-10019.
3. L. Artiglia, J. Edebeli, F. Orlando, S. Chen, M.-T. Lee, P. Corral Arroyo, A. Gilgen, T. Bartels-Rausch, A. Kleibert, M. Vazdar, M. Andres Carignano, J. S. Francisco, P. B. Shepson, I. Gladich and M. Ammann, *Nature Communications*, 2017, 8, 700.
4. J. A. Schmidt, D. J. Jacob, H. M. Horowitz, L. Hu, T. Sherwen, M. J. Evans, Q. Liang, R. M. Suleiman, D. E. Oram, M. Le Breton, C. J. Percival, S. Wang, B. Dix and R. Volkamer, *Journal of Geophysical Research: Atmospheres*, 2016, 121, 11,819-811,835.
5. L. Zhu, Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Wang, X., Sherwen, T., Evans, M. and C. J., Q., Alexander, B., Koenig, T. K., Volkamer, R., Huey, L. G., Le Breton, M., Bannan, T. J. and Percival, C. J., *Atmospheric Chemistry and Physics*, 2019, 19, 6497-6507.
6. A. Saiz-Lopez, J. M. C. Plane, A. R. Baker, L. J. Carpenter, R. von Glasow, J. C. Gómez Martín, G. McFiggans and R. W. Saunders, *Chem. Rev. (Washington, DC, U. S.)*, 2012, 112, 1773-1804.
7. R. von Glasow, and Crutzen, P. J. , *Tropospheric Halogen Chemistry* 2007, 4, 1-67.
8. A. K. Luhar, Galbally, I. E., Woodhouse, M. T. and Thatcher, M. , *Atmospheric Chemistry and Physics*, 2017, 17, 3749.
9. Y. Wang and D. J. Jacob, *Journal of Geophysical Research: Atmospheres*, 1998, 103, 31123-31135.
10. A. Saiz-Lopez, Fernandez, R. P., Ordóñez, C., Kinnison, D. E., Gómez Martín, J. C., Lamarque, J. F., and Tilmes, S., *Atmospheric Chemistry and Physics*, 2014, 14, 13119-13143.
11. S. A. Montzka, Reimannander, S., Engel, A., Kruger, O'Doherty, S. K., Sturges, W. T., ... and Kreher, K. , *Ozone-Depleting Substances (ODSs) and Related Chemicals, Chapter 1 in Scientific Assessment of Ozone Depletion*, NIST Report 52, World Meteorological Organization, Geneva, Switzerland, 2010.

12.   A. A. P. Pszenny, W. C. Keene, D. J. Jacob, S. Fan, J. R. Maben, M. P. Zetwo, M. Springer-Young and J. N. Galloway, *Geophysical Research Letters*, 1993, 20, 699-702.

13.   A. S. Mahajan, L. Tinel, A. Sarkar, R. Chance, L. J. Carpenter, S. Hulswar, P. Mali, S. Prakash and P. N. Vinayachandran, *Journal of Geophysical Research: Atmospheres*, 0.

14.   W. L. Chameides and D. D. Davis, *Journal of Geophysical Research: Oceans*, 1980, 85, 7383-7398.

15.   R. von Glasow, von Kuhlmann, R., Lawrence, M. G., Platt, U., and Crutzen, P. J., *Atmos. Chem. Phys.*, 2004, 2481-2497.

16.   A. Saiz-Lopez and R. von Glasow, *Chemical Society Reviews*, 2012, 41, 6448-6472.

17.   T. Sherwen, Evans, M. J., Carpenter, L. J., Schmidt, J. A. and Mickley, L. J, *Atmos. Chem. Phys.*, 2017, DOI: https://doi.org/10.5194/acp-17-1557-2017, 1557-1569.

18.   A. Saiz-Lopez, S. Baidar, C. A. Cuevas, T. K. Koenig, R. P. Fernandez, B. Dix, D. E. Kinnison, J.-F. Lamarque, X. Rodriguez-Lloveras, T. L. Campos and R. Volkamer, *Geophysical Research Letters*, 2015, 42, 6852-6859.

19.   R. J. Salawitch, D. K. Weisenstein, L. J. Kovalenko, C. E. Sioris, P. O. Wennberg, K. Chance, M. K. W. Ko and C. A. McLinden, *Geophysical Research Letters*, 2005, 32.

20.   B.-M. Sinnhuber and S. Meul, *Geophysical Research Letters*, 2015, 42, 2449-2456.

21.   Q. Chen, J. A. Schmidt, V. Shah, L. Jaeglé, T. Sherwen and B. Alexander, *Geophysical Research Letters*, 2017, 44, 7069-7078.

22.   W. J. Bloss, J. D. Lee, G. P. Johnson, R. Sommariva, D. E. Heard, A. Saiz-Lopez, J. M. C. Plane, G. McFiggans, H. Coe, M. Flynn, P. Williams, A. R. Rickard and Z. L. Fleming, *Geophysical Research Letters*, 2005, 32.

23.   C. D. O'Dowd, J. L. Jimenez, R. Bahreini, R. C. Flagan, J. H. Seinfeld, K. Hämeri, L. Pirjola, M. Kulmala, S. G. Jennings and T. Hoffmann, *Nature*, 2002, 417, 632-636.

24.   H. M. Atkinson, R. J. Huang, R. Chance, H. K. Roscoe, C. Hughes, B. Davison, A. Schönhardt, A. S. Mahajan, A. Saiz-Lopez, T. Hoffmann and P. S. Liss, *Atmos. Chem. Phys.*, 2012, 12, 11229-11244.

25.   J. D. Allan, P. I. Williams, J. Najera, J. D. Whitehead, M. J. Flynn, J. W. Taylor, D. Liu, E. Darbyshire, L. J. Carpenter, R. Chance, S. J. Andrews, S. C. Hackenberg and G. McFiggans, *Atmos. Chem. Phys.*, 2015, 15, 5599-5609.

26.   H. K. Roscoe, A. E. Jones, N. Brough, R. Weller, A. Saiz-Lopez, A. S. Mahajan, A. Schoenhardt, J. P. Burrows and Z. L. Fleming, *J. Geophys. Res.: Atmos.*, 2015, 120, 7144-7156.

27.   R. Atkinson, Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J., *Atmos. Chem. Phys.*, 2008, DOI: https://doi.org/10.5194/acp-8-4141-2008, 4141-4496.

28.   J. Wright, *Seawater: its composition, properties, and behaviour* 1995.

29.   E. R. Lewis, Lewis, E. R., Lewis, R., and Schwartz, S. E., *Sea salt aerosol production: mechanisms, methods, measurements, and models*, 2004.

30.   C. D. O'Dowd, M. C. Facchini, F. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y. J. Yoon and J.-P. Putaud, *Nature*, 2004, 431, 676.

31.   N. W. Oldridge and J. P. D. Abbatt, *J. Phys. Chem. A*, 2011, 115, 2590-2598.

32.   J. A. Garland and H. Curtis, *Journal of Geophysical Research: Oceans*, 1981, 86, 3183-3186.

33.   K. A. Read, A. S. Mahajan, L. J. Carpenter, M. J. Evans, B. V. E. Faria, D. E. Heard, J. R. Hopkins, J. D. Lee, S. J. Moller, A. C. Lewis, L. Mendes, J. B. McQuaid, H. Oetjen, A. Saiz-Lopez, M. J. Pilling and J. M. C. Plane, *Nature*, 2008, 453, 1232-1235.

34.   Y. Sakamoto, A. Yabushita, M. Kawasaki and S. Enami, *J. Phys. Chem. A*, 2009, 113, 7707-7713.

35.   D. I. Reeser and D. J. Donaldson, *Atmos. Environ.*, 2011, 45, 6116-6120.

36.   S. N. Wren and D. J. Donaldson, *PCCP*, 2010, 12, 2648-2654.

37.   S. Hayase, A. Yabushita, M. Kawasaki, S. Enami, M. R. Hoffmann and A. J. Colussi, *J. Phys. Chem. A*, 2010, 114, 6016-6021.

38.   S. Hayase, A. Yabushita and M. Kawasaki, *J. Phys. Chem. A*, 2012, 116, 5779-5783.

39. S. Hayase, A. Yabushita, M. Kawasaki, S. Enami, M. R. Hoffmann and A. J. Colussi, *The Journal of Physical Chemistry A*, 2011, 115, 4935-4940.

40. C. G. Moreno, O. Gálvez, V. López-Arza Moreno, E. M. Espildora-García and M. T. Baeza-Romero, *Physical Chemistry Chemical Physics*, 2018, 20, 27571-27584.

41. A. S. Mahajan, L. Tinel, A. Sarkar, R. Chance, L. J. Carpenter, S. Hulswar, P. Mali, S. Prakash and P. N. Vinayachandran, *Journal of Geophysical Research: Atmospheres*, 2019, 0.

42. R. A. Duce, J. T. Wasson, J. W. Winchester and F. Burns, *Journal of Geophysical Research (1896-1977)*, 1963, 68, 3943-3947.

43. J. L. Moyers and R. A. Duce, *Journal of Geophysical Research (1896-1977)*, 1972, 77, 5229-5238.

44. R. Sander, Keene, W. C., Pszenny, A. A. P., Arimoto, R., Ayers, G. P., Baboukas, E., Cainey, J. M., Crutzen, P. J., Duce, R. A., Hönninger, G., Huebert, B. J., Maenhaut, W., Mihalopoulos, N., Turekian, V. C., and Van Dingenen, R., *Atmos. Chem. Phys.*, 2003, DOI: https://doi.org/10.5194/acp-3-1301-2003, 1301-1336.

45. J. T. Newberg, B. M. Matthew and C. Anastasio, *Journal of Geophysical Research: Atmospheres*, 2005, 110.

46. Y. Sakamoto, M. Goda and J. Hirokawa, *The Journal of Physical Chemistry A*, 2018, 122, 2723-2731.

47. J. A. Garland, A. W. Elzerman and S. A. Penkett, *J. Geophys. Res.: Oceans*, 1980, 85, 7488-7492.

48. L. Piatkowski, Z. Zhang, E. H. G. Backus, H. J. Bakker and M. Bonn, *Nat. Commun.*, 2014, 5, 4083.

49. S. Ghosal, J. C. Hemminger, H. Bluhm, B. S. Mun, E. L. D. Hebenstreit, G. Ketteler, D. F. Ogletree, F. G. Requejo and M. Salmeron, *Science*, 2005, 307, 563-566.

50. P. Jungwirth and D. J. Tobias, *Chemical Reviews*, 2006, 106, 1259-1281.

51. D. J. Tobias, A. C. Stern, M. D. Baer, Y. Levin and C. J. Mundy, in *Annu. Rev. Phys. Chem., Vol 64*, eds. M. A. Johnson and T. J. Martinez, 2013, vol. 64, pp. 339-359.

52. J. P. D. Abbatt and G. C. G. Waschewsky, *The Journal of Physical Chemistry A*, 1998, 102, 3719-3725.

53. R. G. Utter, J. B. Burkholder, C. J. Howard and A. R. Ravishankara, *The Journal of Physical Chemistry*, 1992, 96, 4973-4979.

54. A. Alebić-Juretić, T. Cvitaš and L. Klasinc, *Chemosphere*, 2000, 41, 667-670.

55. L. R. B. Yeatts and H. Taube, *Journal of the American Chemical Society*, 1949, 71, 4100-4105.

56. J. Hoigné, H. Bader, W. R. Haag and J. Staehelin, *Water Research*, 1985, 19, 993-1004.

57. A. V. Levanov, I. V. Kuskov, A. V. Zosimov, E. E. Antipenko and V. V. Lunin, *Kinetics and Catalysis*, 2003, 44, 740-746.

58. Q. Liu, L. M. Schurter, C. E. Muller, S. Aloisio, J. S. Francisco and D. W. Margerum, *Inorg. Chem.*, 2001, 40, 4436-4442.

59. M. Ammann, U. Poschl and Y. Rudich, *PCCP*, 2003, 5, 351-356.

60. B. J. Finlayson-Pitts and J. N. Pitts Jr, *Chemistry of the upper and lower atmosphere: theory, experiments, and applications*, Academic press, 1999.

61. D. R. Hanson, *The Journal of Physical Chemistry B*, 1997, 101, 4998-5001.

62. P. Davidovits, C. E. Kolb, L. R. Williams, J. T. Jayne and D. R. Worsnop, *Chemical Reviews*, 2006, 106, 1323-1354.

63. S. W. Hunt, M. Roeselová, W. Wang, L. M. Wingen, E. M. Knipping, D. J. Tobias, D. Dabdub and B. J. Finlayson-Pitts, *The Journal of Physical Chemistry A*, 2004, 108, 11559-11572.

64. L. Magi, F. Schweitzer, C. Pallares, S. Cherif, P. Mirabel and C. George, *J. Phys. Chem. A*, 1997, 101, 4943-4949.

65. J. H. Hu, Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser and C. E. Kolb, *J. Phys. Chem.*, 1995, 99, 8768-8776.

66. I. Gladich, P. B. Shepson, M. A. Carignano and I. Szleifer, *J. Phys. Chem. A*, 2011, 115, 5895-5899.

67.   S. Naumov and C. von Sonntag, *Ozone: Science & Engineering*, 2008, 30, 339-343.
68.   Ó. Gálvez, M. Teresa Baeza-Romero, M. Sanz and L. F. Pacios, *Physical Chemistry Chemical Physics*, 2016, 18, 7651-7660.
69.   C. Von Sonntag, and Von Gunten, U., *Chemistry of ozone in water and wastewater treatment*, Chemistry of ozone in water and wastewater treatment edn., 2012.
70.   S. Enami, C. D. Vecitis, J. Cheng, M. R. Hoffmann and A. J. Colussi, *The Journal of Physical Chemistry A*, 2007, 111, 8749-8752.
71.   R. Teiwes, J. Elm, M. Bilde and H. B. Pedersen, *Physical Chemistry Chemical Physics*, 2019, DOI: 10.1039/c9cp01734h.
72.   P. V. Danckwerts, and Lannus, A., *Journal of The Electrochemical Society*, 1970, 117, 369C-370C.
73.   P. V. Danckwerts, *Transactions of the faraday society*, 1951, 47, 1014-1023.
74.   D. R. Hanson, A. R. Ravishankara and S. Solomon, *Journal of Geophysical Research: Atmospheres*, 1994, 99, 3615-3629.
75.   M. D. Shaw and L. J. Carpenter, *Environmental Science & Technology*, 2013, 47, 10947-10954.
76.   P. Jungwirth and D. J. Tobias, *J. Phys. Chem. B*, 2001, 105, 10468-10472.
77.   S. M. MacDonald, J. C. Gómez Martín, R. Chance, S. Warriner, A. Saiz-Lopez, L. J. Carpenter and J. M. C. Plane, *Atmos. Chem. Phys.*, 2014, 14, 5841-5852.
78.   S. Weisenberger and A. Schumpe, *AIChE J.*, 1996, 42, 298-300.
79.   E. Rischbieter, H. Stein and A. Schumpe, *Journal of Chemical & Engineering Data*, 2000, 45, 338-340.
80.   C. C. Miller and J. Walker, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 1924, 106, 724-749.
81.   P. N. Johnson and R. A. Davis, *Journal of Chemical & Engineering Data*, 1996, 41, 1485-1487.
82.   R. Tamamushi and T. Isono, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 1984, 80, 2751-2758.
83.   W. J. Hamer and Y. C. Wu, *Journal of Physical and Chemical Reference Data*, 1972, 1, 1047-1100.
84.   R. C. Beckwith, T. X. Wang and D. W. Margerum, *Inorganic Chemistry*, 1996, 35, 995-1000.
85.   W. R. Haag and J. Hoigne, *Environmental Science & Technology*, 1983, 17, 261-267.
86.   T. X. Wang, M. D. Kelley, J. N. Cooper, R. C. Beckwith and D. W. Margerum, *Inorganic Chemistry*, 1994, 33, 5872-5878.
87.   M. Eigen and K. Kustin, *Journal of the American Chemical Society*, 1962, 84, 1355-1361.
88.   I. Lengyel, I. R. Epstein and K. Kustin, *Inorg. Chem.*, 1993, 32, 5880-5882.
89.   Y. Bischel and U. von Gunten, *Water Res.*, 2000, 34, 3197-3203.
90.   Y. L. Wang, J. C. Nagy and D. W. Margerum, *Journal of the American Chemical Society*, 1989, 111, 7838-7844.
91.   D. W. Margerum, P. N. Dickson, J. C. Nagy, K. Kumar, C. P. Bowers and K. D. Fogelman, *Inorganic Chemistry*, 1986, 25, 4900-4904.
92.   R. de Barros Faria, Lengyel, I., Epstein, I. R., and Kustin, K. , *Journal of physical chemistry*, 1993, 97, 1164-1171.
93.   R. C. Troy, M. D. Kelley, J. C. Nagy and D. W. Margerum, *Inorganic Chemistry*, 1991, 30, 4838-4845.
94.   R. von Glasow, R. Sander, A. Bott and P. J. Crutzen, *Journal of Geophysical Research: Atmospheres*, 2002, 107, ACH 9-1-ACH 9-16.
95.   C. N. Hinshelwood, *The kinetics of chemical change*, 1940.
96.   K. J. Laidler, S. Glasstone and H. Eyring, *The Journal of Chemical Physics*, 1940, 8, 659-667.
97.   B. T. Mmereki and D. J. Donaldson, *The Journal of Physical Chemistry A*, 2003, 107, 11038-11042.
98.   B. T. Mmereki, D. J. Donaldson, J. B. Gilman, T. L. Eliason and V. Vaida, *Atmospheric Environment*, 2004, 38, 6091-6103.

99. U. Pöschl, T. Letzel, C. Schauer and R. Niessner, *The Journal of Physical Chemistry A*, 2001, 105, 4029-4041.

100. T. Berkemeier, S. S. Steimer, U. K. Krieger, T. Peter, U. Pöschl, M. Ammann and M. Shiraiwa, *Physical Chemistry Chemical Physics*, 2016, 18, 12662-12674.

101. P. Nissenson, L. M. Wingen, S. W. Hunt, B. J. Finlayson-Pitts and D. Dabdub, *Atmospheric Environment*, 2014, 89, 491-506.

102. D. Clifford, D. J. Donaldson, M. Brigante, B. D'Anna and C. George, *Environmental Science & Technology*, 2008, 42, 1138-1143.

103. S. Ou and S. Patel, *The Journal of Physical Chemistry B*, 2013, 117, 6512-6523.

104. K. Christmann, ed. S. S. B. Media, 2013, vol. 1.

105. M. Antalek, E. Pace, B. Hedman, K. O. Hodgson, G. Chillemi, M. Benfatto, R. Sarangi and P. Frank, *The Journal of Chemical Physics*, 2016, 145, 044318.

106. A. Rouvière, Y. Sosedova and M. Ammann, *J. Phys. Chem. A*, 2010, 114, 7085-7093.

107. M. Schutze and H. Herrmann, *PCCP*, 2002, 4, 60-67.

108. M.-T. Lee, M. A. Brown, S. Kato, A. Kleibert, A. Türler and M. Ammann, *The Journal of Physical Chemistry A*, 2015, 119, 4600-4608.

109. M. Mekic, G. Loisel, W. Zhou, B. Jiang, D. Vione and S. Gligorovski, *Environmental Science & Technology*, 2018, 52, 12306-12315.

110. R. S. Disselkamp, E. G. Chapman, W. R. Barchet, S. D. Colson and C. D. Howd, *Geophysical Research Letters*, 1999, 26, 2183-2186.

111. S. N. Wren, T. F. Kahan, K. B. Jumaa and D. J. Donaldson, *Journal of Geophysical Research: Atmospheres*, 2010, 115.

112. J. Edebeli, M. Ammann and T. Bartels-Rausch, *Environmental Science: Processes & Impacts*, 2019, 21, 63-73.

113. C. Anastasio and M. Mozurkewich, *Journal of Atmospheric Chemistry*, 2002, 41, 135-162.

114. P. Nissenson, D. M. Packwood, S. W. Hunt, B. J. Finlayson-Pitts and D. Dabdub, *Atmospheric Environment*, 2009, 43, 3951-3962.

115. J. L. Thomas, A. Jimenez-Aranda, B. J. Finlayson-Pitts and D. Dabdub, *The Journal of Physical Chemistry A*, 2006, 110, 1859-1867.

116. I. Gladich, J. S. Francisco, R. J. Buszek, M. Vazdar, M. A. Carignano and P. B. Shepson, *The Journal of Physical Chemistry A*, 2015, 119, 4482-4488.

117. I. Langmuir, *Journal of the American Chemical Society*, 1916, 38, 2221-2295.

118. N. Ottosson, J. Heyda, E. Wernersson, W. Pokapanich, S. Svensson, B. Winter, G. Öhrwall, P. Jungwirth and O. Björneholm, *Physical Chemistry Chemical Physics*, 2010, 12, 10693-10700.

119. S. Enami, H. Mishra, M. R. Hoffmann and A. J. Colussi, *The Journal of Chemical Physics*, 2012, 136, 154707.

120. P. Jungwirth and D. J. Tobias, *J. Phys. Chem. B*, 2002, 106, 6361-6373.

121. S. Ghosal, M. A. Brown, H. Bluhm, M. J. Krisch, M. Salmeron, P. Jungwirth and J. C. Hemminger, *J. Phys. Chem. A*, 2008, 112, 12378-12384.

122. P. B. Petersen and R. J. Saykally, in *Annu. Rev. Phys. Chem.*, 2006, vol. 57, pp. 333-364.

123. B. G. Ershov, M. Kelm, A. V. Gordeev and E. Janata, *Physical Chemistry Chemical Physics*, 2002, 4, 1872-1875.

124. F. J. Millero, *Chemical oceanography*, 2011.

125. N. Ottosson, L. Cwiklik, J. Söderström, O. Björneholm, G. Öhrwall and P. Jungwirth, *The Journal of Physical Chemistry Letters*, 2011, 2, 972-976.

126. S. Enami, M. R. Hoffmann and A. J. Colussi, *The Journal of Physical Chemistry Letters*, 2010, 1, 1599-1604.

127. P. Jungwirth, J. E. Curtis and D. J. Tobias, *Chemical Physics Letters*, 2003, 367, 704-710.

128. H. Taube, *Journal of the American Chemical Society*, 1942, 64, 2468-2474.

129. K. Haruta and T. Takeyama, *The Journal of Physical Chemistry*, 1981, 85, 2383-2388.

130. J. Cheng, C. D. Vecitis, M. R. Hoffmann and A. J. Colussi, *The Journal of Physical Chemistry B*, 2006, 110, 25598-25602.
131. U. Pöschl, Y. Rudich and M. Ammann, *Atmos. Chem. Phys.*, 2007, 7, 5989-6023.
132. C. Pilinis and J. H. Seinfeld, *Atmospheric Environment (1967)*, 1987, 21, 2453-2466.
133. L. Renbaum-Wolff, J. W. Grayson, A. P. Bateman, M. Kuwata, M. Sellier, B. J. Murray, J. E. Shilling, S. T. Martin and A. K. Bertram, *Proceedings of the National Academy of Sciences*, 2013, 110, 8014-8019.
134. R. M. Power, S. H. Simpson, J. P. Reid and A. J. Hudson, *Chemical Science*, 2013, 4, 2597-2604.
135. L. N. Ganzeveld, D. Helmig, C. W. Fairall, J. Hare and A. Pozzer, *Global Biogeochemical Cycles*, 2009, 23.
136. D. I. Reeser, A. Jammoul, D. Clifford, M. Brigante, B. D'Anna, C. George and D. J. Donaldson, *The Journal of Physical Chemistry C*, 2009, 113, 2071-2077.
137. T. Loegager, J. Holcman, K. Sehested and T. Pedersen, *Inorganic Chemistry*, 1992, 31, 3523-3529.
138. F. Jacobsen, J. Holcman and K. Sehested, *International Journal of Chemical Kinetics*, 1998, 30, 215-221.
139. M. J. Krisch, R. D'Auria, M. A. Brown, D. J. Tobias, C. Hemminger, M. Ammann, D. E. Starr and H. Bluhm, *The Journal of Physical Chemistry C*, 2007, 111, 13497-13509.
140. M.-T. Lee, F. Orlando, M. Khabiri, M. Roeselová, M. A. Brown and M. Ammann, *Physical Chemistry Chemical Physics*, 2019, 21, 8418-8427.
141. S. Enami, M. R. Hoffmann and A. J. Colussi, *ACS Omega*, 2019, 4, 7574-7580.
142. M. I. Guzman, R. R. Athalye and J. M. Rodriguez, *The Journal of Physical Chemistry A*, 2012, 116, 5428-5435.
143. S. Pechtl, G. Schmitz and R. von Glasow, *Atmos. Chem. Phys.*, 2007, 7, 1381-1393.
144. R. W. Saunders, R. Kumar, S. M. MacDonald and J. M. C. Plane, *Environmental Science & Technology*, 2012, 46, 11854-11861.
145. M. Z. Jacobson, *Journal of Geophysical Research: Atmospheres*, 2005, 110.
146. J. Werner, M. Dalirian, M.-M. Walz, V. Ekholm, U. Wideqvist, S. J. Lowe, G. Öhrwall, I. Persson, I. Riipinen and O. Björneholm, *Environmental Science & Technology*, 2016, 50, 7434-7442.