A revisit of the interaction of gaseous ozone with aqueous iodide. Estimating the contributions of the surface and bulk reactions

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The main source of atmospheric iodine is the heterogeneous reaction of aqueous iodide (I\(^-\)) with ozone (O\(_3\)), which takes place in surface seawater and probably in sea-salt aerosols. However, there are seemingly contradictory conclusions about whether this heterogeneous reaction occurs in the bulk of the aqueous phase, via O\(_3\) dissolution, or at the aqueous surface, via O\(_3\) adsorption. In this work, the ozone uptake coefficient has been calculated as a function of the concentration of aqueous iodide ([I\(^-\)]\(_a\)) and gaseous ozone near the aqueous surface ([O\(_3\)]\(_g\)) by estimating parameters of the resistor model using results of previous studies. The calculated uptake coefficients suggest that the aqueous-phase reaction dominates at low I\(^-\) concentrations (about <10\(^-4\) mol/L), regardless of [O\(_3\)]\(_g\), and also at sufficiently high [O\(_3\)]\(_g\), (about >10 ppm), regardless of [I\(^-\)]\(_a\). In contrast, the surface reaction dominates at high [I\(^-\)]\(_a\) (about >10\(^-1\) mol/L) as long as [O\(_3\)]\(_g\) is low enough (about <10 ppm). This trend is able to reconcile previous studies of this reaction, and is a consequence of several factors, including the high surface excess of both reactants ozone and iodide. Given the typical O\(_3\) concentrations in the troposphere and the possible I\(^-\) concentrations and O\(_3\) solubilities in sea-salt aerosols, the surface reaction may compete with the aqueous phase reaction in sea-salt aerosols, unlike in surface seawater, where the aqueous-phase reaction prevails. The rate constant of the surface reaction has been estimated as \((5-500)\times10^{-13}\) cm\(^2\) molecule\(^{-1}\) s\(^{-1}\).

Introduction

The reaction of aqueous iodide (I\(^-\)) with gaseous ozone (O\(_3\)) releases iodine from surface seawater as hypooiodic acid (HOI) and molecular iodine (I\(_2\)).\(^1\)\(^-\)\(^3\) In the atmosphere, iodine destroys ozone catalytically, possibly accounting for 18% of tropospheric O\(_3\) loss,\(^5\) thereby cleaning the air in marine areas and reducing the warming effect that ozone causes.\(^4\)\(^,\)\(^5\) Atmospheric iodine is important for climate as well due to its potential to form ultrafine particles that act as cloud condensation nuclei (CCN).\(^6\)\(^-\)\(^9\) Moreover, iodine has an important role in controlling the atmospheric oxidative capacity since it influences the concentration of HO\(_x\) and NO\(_x\).\(^3\)\(^,\)\(^10\) The reaction I\(^-\)+O\(_3\) could also take place in marine aerosols, whose speciation of iodine is not well understood.\(^6\)\(^,\)\(^11\)\(^,\)\(^12\) In fact, there are many gaps in the knowledge of both the aqueous- and gas-phase chemistry of iodine.\(^11\)\(^,\)\(^13\)

Despite the importance of the reaction I\(^-\)+O\(_3\) as the main source of atmospheric iodine,\(^1\)\(^-\)\(^14\) the mechanism of this reaction has not been completely clarified. While several authors have inferred that the reaction follows classical aqueous-phase kinetics via previous solvation of O\(_3\),\(^1\)\(^5\)\(^-\)\(^18\) other authors\(^19\)\(^-\)\(^24\) have concluded that it takes place at the surface of aqueous solutions or particles via adsorption of O\(_3\), following Langmuir- Hinshelwood kinetics. The possibility that both pathways coexist has also been suggested.\(^18\)

The aqueous-phase reaction\(^25\) pathway can be described by the following consecutive processes:

\[O_3(g) \leftrightarrow O_3(aq)\]  \hspace{1cm} (R1)

\[O_3(aq) \leftrightarrow O_3(aq)\]  \hspace{1cm} (R2)

\[O_3(aq) + I^- (aq) \rightarrow IO_3^- (aq)\]  \hspace{1cm} (R3)

where O\(_3\)(aq) is ozone in the gas phase bulk, O\(_3\)(aq) is gaseous ozone near the aqueous surface, and O\(_3\)(aq), I\(^-\)(aq) and IO\(_3\)(aq) are aqueous ozone, iodide and hypooiodite, respectively. Due to the competing processes of resistance to O\(_3\) diffusion in the aqueous phase and O\(_3\) consumption by reaction, the aqueous-phase reaction pathway leads to an ozone concentration gradient in the aqueous phase. However, the reaction is so fast that aqueous O\(_3\) diffusion is scarcely competitive and most of the aqueous-phase reaction takes place relatively close the
surface.1,15 Throughout this work, this pathway will be referred indistinctively as “aqueous phase” or “bulk” reaction pathway.

The Langmuir-Hinshelwood reaction pathway can be formulated as follows:22

\[
\begin{align*}
O_3(g) &\leftrightarrow O_3(g)_{\text{ads}} \quad (R1) \\
O_3(g) + \text{site} &\leftrightarrow O_3(\text{surf}) \quad (R4) \\
O_3(\text{surf}) + I_{\text{int}} &\rightarrow IO_3^-_{\text{int}} \quad (R5)
\end{align*}
\]

where “site” is a region of the surface where a single molecule of \( \text{O}_3 \) can adsorb, \( O_3(\text{surf}) \) is ozone adsorbed on the aqueous surface, and \( I_{\text{int}} \) and \( IO_3^-_{\text{int}} \) are the concentration of iodide and hypoiodite at the aqueous surface, respectively. Except at high pH (>10), the main final product of either reaction R3 or R5 is not IO• but it is its protonated form HOI or I\(_2\) produced through some consecutive equilibrium reactions.22

Because the aqueous-phase reaction between ozone and iodide involves \( O_3(\text{ads}) \) (dissolved \( \text{O}_3 \)), it strongly depends on the \( \text{O}_3 \) solubility. On the other hand, the Langmuir-Hinshelwood reaction involves \( O_3(\text{surf}) \) (adsorbed \( \text{O}_3 \)) and it therefore depends on the number of surface sites per surface area, or \( \mathcal{S} / \mathcal{R} \) (where \( \mathcal{S} \) is the effective cross section of an adsorbed \( \text{O}_3 \) molecule), and on the tendency of \( \text{O}_3 \) to adsorb on those sites, which is expressed through the adsorption equilibrium constant of ozone (\( K_{\text{O}_3} \)). Ozone has in fact been found to adsorb onto aqueous and liquid surfaces according to a Langmuir isotherm,26,27 which is described by the following equation:28

\[
[O_3]_{\text{surf}} = \frac{K_{\text{O}_3}[O_3]_{\text{gs}}}{\mathcal{S} (1 + K_{\text{O}_3}[O_3]_{\text{gs}})} \quad (1)
\]

where \([O_3]_{\text{surf}}\) is the concentration of adsorbed ozone and \([O_3]_{\text{gs}}\) is the concentration of gaseous ozone near the aqueous surface. From equation 1 it can be inferred that the rate of \( \text{O}_3 \) surface reactions reaches a limit at high \( \text{O}_3 \) concentrations due to surface saturation of \( \text{O}_3 \). Not only ozone, but also iodide has also been found to adsorb to the surface obeying a Langmuir isotherm, which in this case is a function of the aqueous-phase concentration.20,23

The resistor model is frequently used to describe the uptake of gas species by atmospheric particles due to its simplicity.28 It is a mass balance for (quasi)-steady-state conditions that decouples the overall process of gas uptake by particles into several stages. These stages may include gas adsorption, bulk accommodation, aqueous-phase reaction, and surface reaction. The kinetics of each decoupled stage is described by a “conductance” (\( \Gamma_{\text{stage}} \) inverse to “resistance”). The overall conductance is called the uptake coefficient (\( \gamma \)) and is defined as the number of gas-particle collisions that lead to gas uptake divided by the number of gas-particle collisions. The uptake coefficient can also be used to describe the kinetics of gas-solution interactions, as it will be done in this work, although in this case it is more frequent to use the gas deposition velocity as an equivalent way of expressing gas consumption.

In the present work we will calculate the uptake coefficient for the interaction of \( \text{O}_3 \) with \( I_{\text{int}} \) particles or solutions as a function of reactant concentrations using known or estimated values of the resistor model parameters in order to explore for which range of \( I^- \) and \( \text{O}_3 \) concentrations each reaction pathway, surface or aqueous-phase, may dominate. Thus, we will attempt to reach a reconciliation among the different results obtained in the studies of this gas-liquid reaction.1,15,16,24,30,31,17

1. Model description

Resistor models of gas uptake by particles or solutions are often simple, especially when several decoupled processes do not need to be considered. In the interaction of ozone with iodide particles or solutions, the conductance of the liquid-phase diffusion is negligible in comparison to the conductance of the aqueous-phase reaction (a parallel pathway) because the former is limited by the low \( \text{O}_3 \) solubility in aqueous solutions,32 and the latter is very high, with a rate constant of 2.10^{-5} \text{L} \text{mol}^{-1} \text{s}^{-1}.15 Furthermore, under some conditions, the aqueous-phase reaction may be dominant over the surface reaction, as some studies1,15-17,18 suggest. In that case the uptake coefficient depends only on two conductances, which are the bulk accommodation of \( \text{O}_3 \) (\( \alpha_b \)) and the aqueous-phase reaction (\( \Gamma_{\text{rxn}} \)):28

\[
\frac{1}{\gamma_{\text{aq}}} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{rxn}}} \quad (2)
\]

where \( \gamma_{\text{aq}} \) is how the uptake coefficient will be denoted throughout this work when the surface reaction is not accounted for. The bulk accommodation of \( \text{O}_3 \) (\( \alpha_b \)) is defined as the number of \( \text{O}_3 \)-particle collisions that lead to \( \text{O}_3 \) solvation divided by the number of \( \text{O}_3 \)-particle collisions. A lower limit for it can be obtained experimentally.16

On the other hand, if the reaction among \( I^- \) and \( \text{O}_3 \) occurs predominantly at the surface via Langmuir-Hinshelwood kinetics, as other studies19-23,32,34 suggest, the uptake coefficient depends on the conductance of surface accommodation (\( \alpha_s \)) and on the conductance of the surface reaction (\( \Gamma_{\text{surf rxn}} \)):29

\[
\frac{1}{\gamma_s} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_{\text{surf rxn}}} \quad (3)
\]

where \( \gamma_s \) is how the uptake coefficient will be denoted throughout the present work when the aqueous phase reaction is not taken into account. The surface accommodation coefficient (\( \alpha_s \)) is defined as the number of gas-particle collisions that lead to adsorption divided by the number of gas-particle collisions, and it therefore must be higher than the bulk accommodation coefficient.33
If both a surface reaction and an aqueous reaction take place among $I_{aq}$ and $O_3$, the expression for the resistor model is slightly more complex:\textsuperscript{29}

$$\frac{1}{Y} = \frac{1}{\alpha_s} + \frac{1}{\alpha_s \frac{k_{vol}}{k_d} + \frac{1}{\Gamma_{surf rxn}}}$$ \hspace{1cm} (4)

where $\gamma$ is the total uptake, $k_{vol}$ is the rate of $O_3$ solvation from the surface, and $k_d$ is the rate of $O_3$ desorption.

In the present work real uptake coefficients ($\gamma_{real}$) will be estimated. It is important to note that these are different from effective, apparent, or net uptake coefficients ($\gamma_{net}$), which are measurable variables that depend on the variation in the gas phase bulk concentration ($[O_3]_g$). In contrast, the real uptake depends on the variation of the gas-phase concentration near the aqueous surface ($[O_3]_{aq}$), which is usually lower than $[O_3]_g$ due to gas-phase resistance. The real and apparent uptake coefficients are related by the following equation:\textsuperscript{33}

$$\frac{1}{\gamma_{eff}} = \frac{1}{\gamma_{real}} + \frac{1}{\Gamma_g}$$ \hspace{1cm} (5)

where $\Gamma_g$ is the conductance of gas-phase diffusion. From equation 5 it follows that gas-phase resistance leads to a reduction of the effective uptake ($\gamma_{real}$). Because the uptake coefficients calculated here will be a function of $[O_3]_{aq}$ (if they depend on the $O_3$ concentration), when applying these coefficients to real conditions it must be kept in mind that $[O_3]_{aq}$ is often lower than $[O_3]_g$. Authors usually calculate effective uptakes by calculating the gas-phase resistance, thus providing real uptakes, which do not depend on the gas phase resistance.

In the rest of this section we will estimate the parameters required for resistor models 2-4 in order to obtain the value of the real uptake coefficient as a function of $[I]_{aq}$ and $[O_3]_{aq}$ for each case: i) dominant aqueous-phase reaction, ii) dominant surface reaction, and iii) simultaneous aqueous-phase and surface reactions.

### 1.1 Aqueous-phase reaction $I_{aq} + O_3(aq)$

Substituting the expression\textsuperscript{29} for the aqueous-phase reaction conductance in equation 2 the following resistor model results when no surface reaction takes place among $I$ and $O_3$:

$$\frac{1}{\gamma_{aq}} = \frac{1}{\alpha_b} + \frac{c}{4s\sqrt{k}[I]_{aq} D_{aq}}$$ \hspace{1cm} (6)

where $[I]_{aq}$ is the iodide concentration in the aqueous phase, $s$ is the non-dimensional gas-to-liquid solubility of $O_3$, $k$ is the second-order rate constant of the reaction of iodide with aqueous ozone, $D_{aq}$ is the diffusivity of $O_3$ in the aqueous phase, and $c$ is the mean thermal velocity of $O_3$ in the gas phase.

Table 1 shows the values selected for the parameters of equation 6. The value selected for the bulk accommodation coefficient ($\alpha_b$) is the lower limit determined by Magi et al.\textsuperscript{16}, who studied ozone uptake by aqueous microdroplets containing 0.5-3 mol L$^{-1}$ of iodide. Although the bulk accommodation coefficient of $O_3$ may depend on the concentration of iodide, as suggested by the different lower limits found for surfaces containing pure water (2.10$^{-3}$) and other aqueous substrates,\textsuperscript{34} a sensitivity analysis demonstrates that this range of uncertainty does not influence the total uptake (see section S2 in the Supplementary Information). We have selected the rate constant ($k$) determined by Garland et al.\textsuperscript{15} at 25 $\degree$C, who used low iodide concentrations, because the rate of this aqueous-phase reaction can be obtained more accurately at low concentrations of $I$, as we argue in the results and discussion section. Shaw and Carpenter\textsuperscript{35} also used low iodide concentrations and obtained a slightly lower rate constant at 20 $\degree$C than Garland et al.\textsuperscript{15} at 25 $\degree$C, suggesting a positive correlation of the rate constant with temperature that is in agreement with Magi et al.’s study.\textsuperscript{16}

**Table 1** Summary of the values of the parameters at about 23$\degree$C required for the resistor model in the case of aqueous-phase reaction dominance (equations 6 and 7).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>2.10$^{-9}$ L mol$^{-1}$ s$^{-1}$</td>
<td>Garland et al.\textsuperscript{15}</td>
</tr>
<tr>
<td>$\alpha_b$</td>
<td>0.1</td>
<td>Magi et al.\textsuperscript{16}</td>
</tr>
<tr>
<td>$D_{aq}$</td>
<td>1.8.10$^{-5}$ cm$^2$ s$^{-1}$</td>
<td>Johnson and Davis\textsuperscript{36}</td>
</tr>
<tr>
<td>$c$</td>
<td>3.5.10$^{-5}$ cm$^2$ s$^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$s_0$</td>
<td>0.274</td>
<td>Gershenzon et al.\textsuperscript{32}</td>
</tr>
<tr>
<td>$h$</td>
<td>1.15.10$^{-4}$ L mol$^{-1}$</td>
<td>Rischbieter et al.\textsuperscript{37}</td>
</tr>
<tr>
<td>$h_{t,\alpha/\kappa}$</td>
<td>0.107 L mol$^{-1}$</td>
<td>Weisenberger and Schumpe\textsuperscript{18} *</td>
</tr>
<tr>
<td>$h_t$</td>
<td>4.10$^{-3}$ L mol$^{-1}$</td>
<td>Weisenberger and Schumpe\textsuperscript{18}</td>
</tr>
</tbody>
</table>

*The average value of $h_{t,\alpha/\kappa}$ and $h_t$ is shown.

The solubility and diffusivity of $O_3$ in pure water also change with temperature, and thus we have selected a temperature value of 23 $\degree$C that is typical among the previous studies of this reaction. The diffusivity of $O_3$ may also change with salt concentration. However, we have ignored this effect because it is difficult to predict and because Magi et al.\textsuperscript{5} measurements of $O_3$ diffusivity in NaI aqueous solutions led them to estimate that $O_3$ diffusivity influences the uptake coefficient by less than 6% in a 3 mol L$^{-1}$ NaI solution with respect to pure water.

The $O_3$ solubility in aqueous media decreases significantly with the concentration of $I$ and other ions at high ionic strengths.\textsuperscript{37} Therefore, the empirical equation of Weisenberger and Schumpe\textsuperscript{18} has been used to predict the $O_3$ solubility in a salt solution ($s$) relative to the $O_3$ solubility in pure water ($s_0$) as a function of salt composition:

$$s/s_0 = 10^{-\sum(h+h_t)c_i}$$ \hspace{1cm} (7)
where \( h \) and \( h \) are parameters specific to each ion present and \( O_3 \), respectively, \( c_i \) is the molar concentration of ion \( i \), and the summation extends over all ions present in the solution. This equation is reliable mostly up to 1.5 mol L\(^{-1}\).\(^{37}\) The parameter \( h \) is a function of temperature and is equal to 1.15 \( \cdot \) 10\(^{-4}\) mol L\(^{-1}\) at 23 °C.\(^{32}\) Values of \( h \) for \( K^+ \), Na\(^+\) (common counter-ions of \( I^- \)), and \( I^- \) are 9.22 \( \cdot \) 10\(^{-2}\), 1.14 \( \cdot \) 10\(^{-1}\), and 3.9 \( \cdot \) 10\(^{-3}\) mol L\(^{-1}\), respectively.\(^{38}\) An average value of \( h \), for \( K^+ \) and Na\(^+\) will be used in order to compare works that have used either of these two counter-ions. The solubility of \( O_3 \) in pure water at 23 °C is 1.1 \( \cdot \) 10\(^{-2}\) M atm\(^{-1}\),\(^{32}\) which is equivalent to a non-dimensional solubility of 0.274 (obtained by dividing the former solubility by RT, where \( R \) is the ideal gas constant and \( T \) is the temperature). Substituting these values in the previous equation (7), the following equation for \( O_3 \) solubility at 23 °C results:

\[
s = 0.274 \cdot 0.782 \frac{[I^-]_{aq}}{(\text{mol L}^{-1})}
\]  

(8)

The mean thermal velocity of \( O_3 \) (c) is defined as \( \sqrt{8RT/\pi M} \), where \( M \) is the molar mass of \( O_3 \). Substituting equation 8 and other required values of Table 1 in equation 6, the following resistor model results when the aqueous-phase reaction of \( I^- \) with \( O_3 \) dominates over the surface reaction:

\[
1/\gamma_{aq} = 10 + \frac{170}{0.782[I^-]_{aq}/(\text{mol L}^{-1})} \left( [I^-]_{aq}/(\text{mol L}^{-1}) \right)^{1/2}
\]  

(9)

The factor 0.782\([I^-]_{aq}/(\text{mol L}^{-1})\) in the previous equation (9) accounts for the decrease in \( O_3 \) solubility in the presence of NaI or KI, as predicted by equation 8. This factor is >0.99 for \([I^-]_{aq}<0.03 \text{ mol L}^{-1}\) and can therefore be ignored in dilute solutions.

### 1.2 Surface reaction \( I^- + O_3, (\text{sur}) \)

Substituting the expression for the conductance of a Langmuir-Hinshelwood reaction in equation 3 the following equation is obtained for the resistor model when the surface reaction among \( I^-_{\text{aq}} \) and \( O_3 \) dominates over the aqueous-phase reaction:

\[
\frac{1}{\gamma_s} = \frac{1}{\alpha_s} + \frac{c \sigma (1 + K_{O_3}[O_3]_{\text{eq}})}{4 K_s [I^-]_{\text{int}} K_{O_3}}
\]  

(10)

where \( K_s \) is the rate constant of the surface reaction. Obtaining a numerical expression for the uptake coefficient \( \gamma_s \) is complicated because several parameters in equation 10 have not been explicitly determined. In addition, the surface concentration of iodide ([I\(^-\)\(_{\text{int}}\)]) must be expressed as a function of the aqueous concentration of iodide ([I\(^-\)\(_{\text{aq}}\)]) in order for equation 10 to be applicable. Therefore, unknown parameters will be estimated using several simplifications and data from literature, and sensitivity analyses of the main uncertain parameters will be made. The values of the parameters needed for this case are explained below and are summarized in Table 2.

The surface accommodation coefficient of \( O_3 (\alpha_i) \) must lie, by definition,\(^{33}\) between the respective bulk accommodation coefficient (0.1)\(^{16}\) and 1. We will adopt the upper limit of 1 arbitrarily because a sensitivity analysis shows that this range of uncertainty only influences uptake when \([I^-]_{aq} > 0.01 \text{ mol L}^{-1}\) and the influence is minor (see Fig S2b Supplementary Information). The effective molecular cross section of \( O_3 (\sigma) \) on water aerosols has been determined by Mmereki and Donaldson\(^{39}\), who studied surface reactions of gaseous organic compounds with \( O_3 \). Although \( \sigma \) could change for a different particle composition, such as one filled with \( I^- \), this possible variation has not been assessed up to date, according to the authors’ knowledge. The inverse of the effective molecular cross section is the maximum concentration of \( O_3 \) at the surface and equals \( 10^{14} \text{ molecule cm}^{-2} \). This is a very high concentration, which can be considered equivalent to >1 mol L\(^{-1}\) if the surface depth is taken as the diameter of \( O_3 \). Taking into account the low solubility of \( O_3 \), such a high maximum concentration of adsorbed \( O_3 \) is expected to play a role in favoring surface reactions of \( O_3 \) (see results and discussion section).

### Table 2 Summary of the values of the parameters at about 23 °C for the resistor model in the case of surface reaction dominance (equations 10-11 and 14).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Reference</th>
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<tbody>
<tr>
<td>( \alpha_i )</td>
<td>1</td>
<td>Estimated</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>1 ( \cdot ) 10(^{-14}) cm(^2) molecule(^{-1})</td>
<td>Mmereki and Donaldson(^{39})</td>
</tr>
<tr>
<td>( K_s )</td>
<td>70 L mol(^{-1})</td>
<td>Reesor and Donaldson(^{20})</td>
</tr>
<tr>
<td>( c_{\text{max}} )</td>
<td>6.4 ( \cdot ) 10(^{21}) molecule cm(^{-2})</td>
<td>Estimated</td>
</tr>
<tr>
<td>( \sigma_2 )</td>
<td>3 ( \cdot ) 10(^{-14}) cm(^2) molecule(^{-2})</td>
<td>Estimated</td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>2 ( \cdot ) 10(^{-14}) cm(^2) molecule(^{-1})</td>
<td>Estimated</td>
</tr>
<tr>
<td>( \alpha_0 )</td>
<td>1 ( \cdot ) 10(^{-17})</td>
<td>Estimated</td>
</tr>
<tr>
<td>( k_s )</td>
<td>To be determined</td>
<td></td>
</tr>
</tbody>
</table>

In order to express the concentration of surface iodide as a function of the aqueous iodide concentration in equation 10, we have examined literature data related to the surface propensity of iodide. Several studies\(^{20,23}\) of the reaction \( I^-_{\text{aq}} + O_3 \) have found a Langmuir relation between the surface and aqueous concentrations of iodide for NaI solutions:

\[
[I^-]_{\text{int}} = \frac{c_{\text{max}} K_{I}[I^-]_{aq}}{1 + K_{I}[I^-]_{aq}}
\]  

(11)

where \( c_{\text{max}} \) is the maximum concentration of \( I^- \) at the surface and \( K_I \) is the adsorption equilibrium constant of \( I^- \) and is a measure of the surface propensity of iodide. The value of \( K_I \) was determined to be 23 L mol\(^{-1}\) and 70 L mol\(^{-1}\) in these studies,\(^{20,23}\) which used iodide concentrations of 5 \( \cdot \) 10\(^{-5}\) to about 0.2 mol L\(^{-1}\).
We will select the latter value because it was determined at neutral pH, which is the pH used by most studies of the reaction of ozone with iodide. Although a study that used second-harmonic generation spectroscopy (SHG) inferred a more extreme propensity of iodide and of other ions for low concentrations (so-called Jones-Ray effect), this has been recently reinterpreted and attributed to a different cause than a high surface propensity of these ions.

According to the authors’ knowledge, the value of the maximum surface concentration of iodide ($c_{max}$) in equation 11 has not been determined. Therefore, in the present work it will be estimated using the surface to aqueous concentration ratio of 3.5 that has been determined for a NaI solution of 3 mol L$^{-1}$ by means of femtosecond-vibrational spectroscopy (SVG). However, this technique measures the surface concentration over a depth of 0.6 nm, which is about twice the depth that is relevant for the surface reaction, since adsorbed O$_3$ is expected to react only with the iodide ions immediately below and iodide has a diameter of 0.36 nm. Thus, the value of $c_{max}$ that will be calculated is only approximate and a sensitivity analysis of this parameter will be presented in the results and discussion. An additional source of error comes from possible differences in the surface propensity of iodide when the present counter-ion is K$^+$ instead of Na$^+$, but these differences may be small according to an SHG study. Furthermore, it is possible that the parameters of equation 10 are different for iodide concentrations >1 mol L$^{-1}$ than for lower concentrations, but we will not consider this possibility because it has not been confirmed and for simplicity.

Because Langmuir-Hinshelwood reactions depend on the surface area available, it is conventional in the literature of these reactions to refer surface concentrations to surface area (molecule cm$^{-2}$) instead of referring them to volume (mol L$^{-1}$). Thus, the concentration determined by Piatkowski et al. (10.5 mol L$^{-1}$) has been divided by the relevant surface depth, which we assume to be equal to the diameter of iodide because only the uppermost layer of iodide ions is expected to reach adsorbed ozone, and necessary conversion of units have been made, yielding a value of [$I$]$_{ads}$=6.3·10$^{24}$ molecule cm$^{-2}$. Substituting this value, $K_r$=70 L mol$^{-1}$, and [$I$]$_{ads}$=3 mol L$^{-1}$, $c_{max}$ is estimated to be 6.4·10$^{21}$ molecule cm$^{-2}$.

Figure 1 shows the surface concentration of iodide as a function of the aqueous concentration of iodide estimated by equation 10 using the parameter values selected above. The surface concentration has been shown in mol L$^{-1}$ units in order to allow comparison with the concentration of aqueous iodide. As it can be seen in this figure, the surface concentration of iodide is 2 orders of magnitude higher than the aqueous phase concentration, except near saturation, and half saturation is reached at an aqueous concentration of about 0.01 mol L$^{-1}$. Such a large difference between the surface and aqueous concentration of iodide is expected to favor the surface reaction over the aqueous phase reaction, at least under some conditions (see results and discussion section).

Ozone adsorption equilibrium constants have been determined for aqueous particles containing diverse compounds, including Br$^-$ and Cl$^-$, and range between 2·10$^{-16}$ and 1·10$^{-12}$ cm$^3$ molecule$^{-1}$. The highest value was obtained for aerosols containing a mixture of NaCl and NaBr, which is also the most relevant in the present study because Cl$^-$ and Br$^-$ are halides, like I$. In the present work we will assume that the adsorption equilibrium constant of O$_3$ for I$^-$ particles ($K_{O3}$) is the same as that for Cl$^-$/Br$^-$ particles due to lack of available data for I$. However, estimating the adsorption equilibrium constant for an iodide solution or particle from the adsorption equilibrium constant determined for Cl$^-$/Br$^-$ particles by Oldridge and Abbatt is not straightforward because this parameter depends on both temperature and surface concentration. The conclusion that the concentration of substrates influences the O$_3$ adsorption equilibrium constant can be drawn by considering that the O$_3$ adsorption equilibrium constant for water surfaces (5·10$^{-16}$ cm$^3$ molecule$^{-1}$) is lower than for NaCl/NaBr and several organic aerosols (about 10$^{-15}$ cm$^3$ molecule$^{-1}$). Therefore, sufficiently dilute I$^-$ particles are expected to have an O$_3$ adsorption equilibrium constant that is equal to that of pure water and that increases linearly with the surface concentration of I$. The procedure used to estimate the adsorption equilibrium constant of O$_3$ for iodide particles or solutions is explained below.

First, as the determined adsorption equilibrium constant of O$_3$ on NaCl/NaBr particles was obtained at a lower temperature than required in the present study, the adsorption equilibrium constant for these particles will be estimated at the temperature of interest (23 °C). The following equation relates the desorption rate constant of ozone ($k_d'$) with temperature:

$$k_d' = A' \cdot \exp(\Delta H' /RT) \quad (12)$$

where we use the superscript ‘ to refer to variables corresponding specifically to the NaCl/NaBr mixture studied by Oldridge and Abbatt, $\Delta H'$ is the enthalpy of adsorption, and $A'$

![Fig. 1 Relation between the surface and aqueous concentration of iodide as predicted by equation 10 using parameter values shown in Table 2.](image-url)
is the preexponential factor. The preexponential factor for adsorption usually ranges between 10^{12} \text{s}^{-1} and 10^{14} \text{s}^{-1}, the upper limit corresponding to high adsorption equilibrium constants.\textsuperscript{26} As O\textsubscript{3} has high adsorption equilibrium constants we will adopt the value of 10^{14} \text{s}^{-1}.\textsuperscript{26} The enthalpy of adsorption ($\Delta H'$) can be obtained from the previous equation together with the relation between the equilibrium constant and the desorption constant at constant temperature:\textsuperscript{28}

$$K_{O_3} (r(0\text{°C})) = \frac{\alpha_s}{4K_d (0\text{°C})^\frac{r}{\sigma}}$$

Substituting $\alpha_s = 0.3$ (estimation made by taking into account the previous discussion about the surface accommodation coefficient of O\textsubscript{3} on an iodide surface), $c_i (0\text{°C}) = 3.4 \times 10^4 \text{ cm}^3 \text {s}^{-1}$, $\sigma = 1.1 \times 10^{-14} \text{ cm}^2$ molecule$^{-1}$, and $K_{O_3}(10\text{°C}) = 1.1 \times 10^{-13} \text{ cm}^3$ molecule$^{-1}$ in the previous equation, a value of 260 s$^{-1}$ is obtained for $k_d(0\text{°C})$. Having estimated this parameter, equation 12 can be applied to obtain $\Delta H' = -61 \text{ K mol}^{-1}$. Applying equations 12-13 again, a value of $1.1 \times 10^{-14} \text{ cm}^3$ molecule$^{-1}$ is estimated for the adsorption equilibrium constant of O\textsubscript{3} for the NaCl/NaBr particles used in the study by Olldridge and Abbatt\textsuperscript{27} ($K_{O_3}(123\text{°C})$). This estimation is not extremely sensitive to neither $\alpha_s$ nor $A'$ between the expected limits of these parameters (0.1-1 and 10^{-12}-10^{-14} \text{ s}^{-1}, respectively). For example, if $A'$ was $10^{12} \text{s}^{-1}$, the constant $K_{O_3}(123\text{°C})$ would be $1.7 \times 10^{-14} \text{ cm}^2$ molecule$^{-1}$.

Having estimated the O\textsubscript{3} adsorption equilibrium constant for a specific surface concentration of Cl and Br ($K_{O_3}(123\text{°C})$), the adsorption equilibrium constant of O\textsubscript{3} as a function of the total surface concentration of halides can be estimated, assuming all of these halides have the same affinity toward O\textsubscript{3} adsorption. In order to do so, the surface concentration of Cl and Br in the previous mixture, whose aqueous phase contains NaCl 0.5 mol L$^{-1}$ and 0.01 mol L$^{-1}$ NaBr,\textsuperscript{27} needs to be estimated. The chloride\textsuperscript{42} and bromide\textsuperscript{45} ions have been determined to have significant surface propensity, but it is not clear how close these ions may lie to the surface boundary. In this study, the relevant surface depth is approximately equal to the ions’ diameter because only ions within this depth are expected to serve as substrate for O\textsubscript{3} adsorption, but studies of surface concentrations usually probe a higher depth or cannot determine the probe depth.\textsuperscript{4245} Therefore, there is uncertainty about the total concentration of halides within the relevant surface region, and we will assume it to be the same as in the bulk (0.5 mol L$^{-1}$). Note that a surface concentration >0 already indicates significant surface propensity (a few decades ago the surface was thought to be depleted of ions).\textsuperscript{44} Finally, dividing the constant $K_{O_3}(123\text{°C})$ by this surface concentration, the adsorption equilibrium constant of ozone per surface mole of halide is estimated to be $2.2 \times 10^{-14} \text{ cm}^3$ molecule$^{-1}$ mol$^{-1}$, except at sufficient dilution, for which the constant is expected to be as for pure water, $5 \times 10^{-16} \text{ cm}^3$ molecule$^{-1}$.\textsuperscript{39} Because the reliability of this estimation is quite uncertain, a sensitivity analysis of its influence on ozone uptake will be presented in the results and discussion section. In order to express $K_{O_3}$ as a function of $[I]_{\text{int}}$, which can be introduced in equation 10, we will use a simple quadratic correlation that approximately satisfies the conditions just specified:

$$K_{O_3}/(\text{cm}^3 \text{molecule}^{-1}) = a_2 [I^-]_{\text{int}}^2 + a_1 [I^-]_{\text{int}} + a_0$$

The values and units of the coefficients $a_2$, $a_1$, and $a_0$ are shown in Table 2.

The rate constant of the surface reaction ($k_i$) has not been determined before. It will be estimated in the next sections by constraining the resistor models here described with results available in literature. The resistor model for surface reaction dominance (equation 10) will be therefore expressed as a function of $[I]_{aq}$, $[O_3]_{ls}$, and $k_i$:

$$\frac{1}{Y_s} = 1 + \frac{1.9 \times 10^{-34} (1 + 70[I^-]_{aq})(1 + K_{O_3}[O_3]_{ls})}{k_i [I^-]_{aq} K_{O_3}}$$

where $[I]_{aq}$ is in mol L$^{-1}$, $k_i$ is in cm$^2$ molecule$^{-1}$ s$^{-1}$, and $K_{O_3}$ is in cm$^3$ molecule$^{-1}$ and is given by equations 11 and 14.

1.3 Simultaneous aqueous-phase and surface reactions

The resistor model for simultaneous aqueous phase and surface reactions (equation 4) only contains as new parameter the solvation to desorption ratio of O\textsubscript{3} ($k_{sol}/k_d$), apart from those required for separate aqueous phase and surface reactions. However, this parameter is not independent but it instead depends on the surface and bulk accommodation coefficients as follows:\textsuperscript{29}

$$\frac{1}{\alpha_b} = \frac{1}{\alpha_s} + \frac{1}{k_d}$$

Substituting $\alpha_b = 0.1$ and $\alpha_s = 1$, the solvation to desorption ratio ($k_{sol}/k_d$) is estimated to be 9, and the following expression for the uptake coefficient is obtained in the case of simultaneous aqueous phase and surface reactions:

$$\frac{1}{Y} = 1 + \frac{\Gamma_{rxn}^{-1} + \Gamma_{surf}^{-1}}{\Gamma_{rxn}} + \Gamma_{surf}$$

where the terms of the reaction conductances have been estimated above as follows:

$$\Gamma_{rxn} = 6.0 \cdot 10^{-3} \cdot 0.782[I^-]_{aq} \cdot \sqrt{[I^-]_{\text{int}}}$$

$$\Gamma_{surf} = \frac{5.2 \times 10^{-33} k_d K_{O_3} [I^-]_{aq}}{(1 + 70[I^-]_{aq})(1 + K_{O_3}[O_3]_{ls})}$$

and where $k_i$ is in cm$^2$ molecule$^{-1}$ s$^{-1}$, $[I]_{aq}$ is in mol L$^{-1}$, and $K_{O_3}$ is given by equations 11 and 14 in cm$^3$ molecule$^{-1}$.\textsuperscript{43}
2. Results and discussion

2.1 Application to previous studies

In this section the uptake coefficients previously calculated will be studied as a function of [I\textsuperscript{−}]\textsubscript{aq} and [O\textsubscript{3}]\textsubscript{gw} for the hypothetical cases of i) aqueous-phase reaction dominance, ii) surface reaction dominance, and iii) simultaneous aqueous-phase and surface reactions. Results will be contrasted with conclusions of previous studies, allowing to estimate a lower limit of the surface reaction rate constant \(k_s\).

Figure 2 shows the estimated uptake coefficients for \([O\textsubscript{3}]\textsubscript{gw}=1\ ppm\) for each of the three considered cases using \(5\times10^{-13}\ \text{cm}^2\text{ molecule}^{-1}\ \text{s}^{-1}\) as surface reaction rate constant. This value is an estimated lower limit whose calculation will be explained in this section. As Figure 2 reveals, at sufficiently low concentrations of iodide (about \(<10^{-4}\ \text{mol L}^{-1}\)), the uptake due to aqueous-phase reaction is greater than that due to surface reaction. This is because the reacto-diffusive length, which is the depth of the aqueous phase through which the majority of dissolved \(O\textsubscript{3}\) diffuses,\textsuperscript{29} is high at low iodide concentrations as a result of a low rate of \(O\textsubscript{3}\) consumption by reaction with I\textsuperscript{−} in the aqueous phase. On the other hand, at high concentrations (about \(>10^{-3}\ \text{mol L}^{-1}\)), the uptake due to surface reaction can surpass the uptake due to aqueous-phase reaction because the volume of the region where the aqueous-phase reaction takes place becomes small due to fast \(O\textsubscript{3}\) consumption by reaction, which does not allow \(O\textsubscript{3}\) to diffuse through a great depth. In addition, the surface reaction is favored by a high surface to aqueous concentration ratio of both I\textsuperscript{−} and \(O\textsubscript{3}\)\textsubscript{g}. Thus, many of the results\textsuperscript{1, 15, 19-23} that have inferred either reaction pathway can be explained by considering the concentration of I\textsuperscript{−} used. Table 3 compares previous works’ conclusions with present conclusions regarding which reaction pathway dominates, some of which need further explanations that are given below.

A few groups\textsuperscript{16, 18, 31} who studied the reaction I\textsubscript{aq} + \(O\textsubscript{3}\) at ambient temperature using high I\textsuperscript{−} concentrations concluded that it occurred in the aqueous phase, in contrast with what has been explained above. The reasons why these studies could have reached a different conclusion than the present one are discussed below.

The conclusions of Magi et al.\textsuperscript{16} may be understood by examining the variation of the uptake coefficient with \([O\textsubscript{3}]\textsubscript{gw}\) for \([I\textsubscript{aq}]=3\ \text{mol L}^{-1}\), which is shown in Figure 3. As it can be seen in this figure, the uptake coefficient due to aqueous-phase reaction becomes higher than the uptake due to surface reaction at sufficiently high concentrations of \([O\textsubscript{3}]\textsubscript{gw} (>10\ ppm)\), the reason being surface saturation of \(O\textsubscript{3}\). It is therefore possible that Magi et al.\textsuperscript{16} used high concentrations of ozone (they did not report the range of ozone concentrations they used). However, the \(O\textsubscript{3}\) uptake obtained by them\textsuperscript{1, 6} (0.013 for \([I\textsubscript{aq}]\textsubscript{gw}=3\ \text{mol L}^{-1}\) is about 2.5 times higher than the uptake predicted to occur for \([O\textsubscript{3}]\textsubscript{gw}=10\ ppm\) by the present model.

Rouviere et al.\textsuperscript{18} did use low concentrations of \(O\textsubscript{3} (<0.3\ ppm)\) and inferred aqueous-phase kinetics, which is in disagreement with present conclusions so far. Ozone and excess iodide concentrations used in their study should result, according to the present model, in a total uptake coefficient that is about 7 times higher than the coefficient they obtained (1.1 \times 10^{-2} for \([O\textsubscript{3}]\textsubscript{gw}=0.1\ \text{ppm}\) and \([I\textsubscript{aq}]=6-7\ \text{mol L}^{-1}\). In addition, the predicted uptake coefficient due to aqueous-phase reaction is 5 \times 10^{-3}, which is about half the value of the coefficient they obtained. These observations suggest that the surface reaction of \(O\textsubscript{3}\) with I\textsuperscript{−} may be, for some reason, partially inhibited under Rouviere et al.’s conditions.

The study of Schutz and Hermann\textsuperscript{31} led these authors to conclude a bulk reaction among iodide and ozone for concentrations >4 \text{ mol L}^{-1} whose order was three. This conclusion was drawn from the type of correlation between the uptake coefficient and \([I\textsubscript{aq}]\) (proportionality between 1/γ and
1/([I]_{aq}). However, it is interesting to note that the same kind of correlation also holds for a second-order surface reaction, as inferred from equation 10.

Table 3 Summary of reactant concentrations used in studies of the reaction $I_{(aq)} + O_3$ studies’ conclusions about whether the reaction takes place at the surface or in the aqueous bulk, and present conclusions.

<table>
<thead>
<tr>
<th>Study</th>
<th>[I]_{aq} / mol L⁻¹</th>
<th>[O₃]_{gs} / ppm</th>
<th>Study’s conclusion about reaction</th>
<th>Present conclusion about reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garland et al.15</td>
<td>$10^{-7}$ – $10^{-5}$</td>
<td>0.1</td>
<td>Bulk</td>
<td>Bulk</td>
</tr>
<tr>
<td>Magi et al.16</td>
<td>0.5 – 3</td>
<td>unknown</td>
<td>Bulk</td>
<td>Bulk</td>
</tr>
<tr>
<td>Liu et al.17</td>
<td>$10^{-5}$ – $10^{-3}$</td>
<td>unknown</td>
<td>Bulk</td>
<td>Bulk</td>
</tr>
<tr>
<td>Schutze and Hermann31</td>
<td>≤ 4</td>
<td>unknown</td>
<td>Bulk</td>
<td>Surface</td>
</tr>
<tr>
<td>Sakamoto et al.22</td>
<td>$10^{-5}$ – $5 \times 10^{-2}$</td>
<td>&lt;300</td>
<td>Surface</td>
<td>Surface</td>
</tr>
<tr>
<td>Wren and Donaldson20</td>
<td>5 $\times 10^{-3}$ – 1</td>
<td>200</td>
<td>Surface</td>
<td>Surface</td>
</tr>
<tr>
<td>Hayase et al.19</td>
<td>1 $\times 10^{-3}$ – 3 $\times 10^{-2}$</td>
<td>20 – 300</td>
<td>Surface</td>
<td>Surface</td>
</tr>
<tr>
<td>Rouviere et al.18</td>
<td>0 – 7</td>
<td>&lt;0.3</td>
<td>Bulk</td>
<td>Surface</td>
</tr>
<tr>
<td>Reeser and Donaldson23</td>
<td>5 $\times 10^{-3}$ – 0.2</td>
<td>&lt;200</td>
<td>Surface</td>
<td>Surface</td>
</tr>
<tr>
<td>Hayase et al.21, 24</td>
<td>(5-30) $\times 10^{-5}$</td>
<td>&lt;200</td>
<td>Surface</td>
<td>Surface</td>
</tr>
<tr>
<td>Carpenter et al.1</td>
<td>$10^{-8}$ – $10^{-6}$</td>
<td>0.07 – 10</td>
<td>Bulk</td>
<td>Bulk</td>
</tr>
</tbody>
</table>

*The aqueous-phase reaction is predicted to dominate in these studies if [O₃]_{gs} is high. Contrarily, the surface reaction is predicted to dominate if [O₃]_{gs} is low.

**The authors of that study31 obtained a correlation between [O₃]_{gs} and [I]_{aq} that indicates either a third order bulk reaction or a second order surface reaction, but the authors did not mention the second possibility.

*The surface reaction in these studies may be partially or totally suppressed in this study as discussed in the text.

*The rate constant of the surface reaction has been constrained with the results of these studies in the present work.

The formation of IO⁻ could be responsible for the seeming absence of the surface reaction under Rouviere et al.’s18 conditions, where 7 M KI nanoparticles were exposed to O₃ for up to 42 s. The product IO⁻, having a bigger size than I⁻, may have more surface propensity than I⁻ and displace I⁻ at the surface,46–48 thus inhibiting the surface reaction. This product is only formed at high pH, because HIO has a high pKₐ,49 and a high pH is only expected to occur when the gas to aqueous-phase volume ratio is high, such as in the case of nanoparticles, iodide concentration is high, and large amounts of O₃ are taken up because interaction times are long. In that case, high iodide conversions can result (>0.1%), converted iodide becomes replaced by the pair of the weak acid HIO, and high concentrations of H⁺ are consumed by this base (IO⁻). In consequence, the surface concentration of iodide may be overestimated for the conditions of this study by the present model, which does not take into account competition of IO⁻ with I⁻ for surface coverage. According to this hypothesis, the surface concentration of iodide is overestimated by one order of magnitude in the present model for Rouviere et al.’s conditions18.

However, if the contribution of the surface reaction to ozone uptake is not accounted for, the present model underpredicts the uptake coefficient for Rouviere et al.’s18 and Magi et al.’s conditions16 in about 2–3 times. The extent of the aqueous-phase reaction is underestimated for the conditions of these studies. The reason for this is likely to be that activities and molar concentrations do not necessarily coincide at high concentrations. In fact, Magi et al.16 predict a higher rate constant than Garland et al.15 and Shaw and Carpenter45, who used low iodide concentrations. In addition, the estimation of the solubility of ozone may be inaccurate at high concentrations of iodide.

The exact O₃ concentration at which the surface and aqueous reactions contribute equally to O₃ uptake depends on I⁻ concentration, but it is not much greater than 10 ppm if the rate constant kₐ is equal to the lower limit given. However, several studies19, 21–23 that used dilute I⁻ solutions and very high O₃(g) concentrations (up to 300 ppm) inferred surface reaction kinetics, which may also seem to disagree with the present analysis because at high O₃ concentrations the surface is expected to be saturated and the aqueous reaction is expected to dominate. However, in those studies, which exposed iodide solutions to ozone, the concentration of gaseous ozone near the surface (O₃(g)) is probably much lower than the ozone concentration in the gas-phase bulk (O₃(g)) due to the high gas-phase resistance that accompanies gas flow over liquid solutions. The ratio [O₃]_{gs}/[O₃]_{surf}, which depends on both the gas-phase resistance and the uptake coefficient, can be estimated by comparing the value of K_{O₃} estimated by equation 14 with the value of the apparent adsorption equilibrium constant (K_{O₃(app)}) that can be determined using production data as a function of [O₃]_{gs}. The Langmuir isotherm of O₃ (equation 1) can be linearized as follows:

$$\frac{[O₃]_{gs}}{[O₃]_{surf}} = \frac{\sigma}{K_{O₃}} + \sigma [O₃]_{gs}$$ (20)
When a surface reaction dominates, I₂ production is proportional to [O₃]surf and therefore [O₃]surf can be substituted by I₂ production multiplied by a constant value in the previous equation. Therefore, by determining the slope and y-intersect of this equation, the value of Kₒₐ can be obtained. However, if [O₃]surf is used instead of [O₃]inst in the equation (because [O₃]surf is unknown), the adsorption constant that is obtained is an apparent one (Kₒₐapp). Therefore, it can be deduced that 

\[ \frac{[O₃]surf}{[O₃]inst} = Kₒₐapp \]

Using this equality and Reeser et al.’s results (specifically, their Figure 1)²³, we have estimated [O₃]surf/[O₃]inst equals 8 × 10⁻³ under their conditions. Thus, the concentration of O₃surf under their conditions is estimated to be <1 ppm and agrees with surface reaction dominance, as Figure 2 shows. For Sakamoto et al.’s conditions²⁸ (Figure 3 in their work), we have estimated the ratio [O₃]surf/[O₃]inst to be 0.07, and thus [O₃]surf<20 ppm (see section S1 in the Supplementary Information).

Introducing the concentrations of O₃surf (0-20 ppm) estimated for Sakamoto et al.’s conditions²⁷ and their iodide concentration (5 × 10⁻³ mol L⁻¹) in the present resistor model (equations 11, 14, 15, 17-19), we have estimated a lower limit for the surface reaction rate constant (kₑ) by imposing that the surface reaction for these concentrations be at least as rapid as the aqueous-phase reaction. The resulting estimation (kₑ=5 × 10⁻¹³ cm² molecule⁻¹ s⁻¹) can be converted to L mol⁻¹ s⁻¹ units by using as surface depth the diameter of iodide in order to compare it with the aqueous-phase reaction rate constant, yielding 10 L mol⁻¹ s⁻¹. Although this rate constant is much lower than the rate constant of the aqueous-phase reaction (2 × 10⁻¹² L mol⁻¹ s⁻¹), the surface reaction is kinetically favored by a high surface to aqueous concentration ratio of both reactants iodide and ozone. For example, for [O₃]surf=0.03 ppm and [I⁻]inst=10⁻⁴ mol L⁻¹, the surface concentration of ozone is estimated to be 1 × 10⁻¹¹ molecule cm⁻², which can be considered equivalent to about 0.06 mol L⁻¹. In contrast, the concentration of aqueous ozone is many orders of magnitude lower (<1 × 10⁻¹⁰ mol L⁻¹), as determined by solubility. This can probably explain why Enami et al.⁵⁰ found that surface iodide in submillimolar NaI microparticles exposed to ozone converted faster than expected for the bulk reaction.

Based on the results here presented, the most reliable way to obtain the rate constant for the aqueous-phase reaction is by using very low I⁻ concentrations (<<10⁻⁴ mol L⁻¹). On the other hand, high I⁻ concentrations ([I⁻]inst > 10⁻⁴ mol L⁻¹) together with sufficiently low O₃ concentrations are required to obtain the rate constant of the surface reaction. The determination of the aqueous-phase rate constant by Magi et al.¹⁶, which was done using high iodide concentrations, might be applied only for high iodide concentrations, for which molar concentrations are expected to be substantially different from activities. However, this determination can be revised with more recent estimations⁵² of salting-out effects on O₃ solubility.

Although the lower limit of the surface reaction rate constant estimated in the present work is very uncertain because it depends on several estimated parameters, the analysis done in the present work provides an explanation for the studies of this heterogeneous reaction. The uncertainties regarding the surface reaction kinetics do not influence the qualitative interpretation and they will be studied in the next section.

2.2 Sensitivity analyses and application of the model to atmospheric conditions

In this section the influence of the parameters whose value is more uncertain are studied. These parameters are the maximum concentration of I⁻ at the surface (cmax), the adsorption equilibrium constant of ozone (Kₒₐ), and the rate constant of the surface reaction (kₑ). These parameters are related to the surface reaction, whose kinetics have not been explicitly modeled before. In addition, an upper limit of the surface reaction rate constant will be estimated.

Figure 4a shows that if the surface could host a higher concentration of I⁻ (in other words, cmax was higher), the surface reaction would dominate at even lower concentrations of I⁻ than for the base case value of cmax. In that case, the lower limit of kₑ estimated in the previous section would decrease. However, the reduction of this lower limit would not be proportional to the increase of cmax because cmax, through its effect on [I⁻]inst, also influences Kₒₐ. For this reason, we have not provided a lower limit of cmax-kₑ as a unified parameter. Figure 4b shows that Kₒₐ also has a significant effect on the surface uptake. This effect is proportional at low O₃ concentrations, which include relevant O₃ tropospheric concentrations, and becomes less important at higher concentrations of ozone due to surface saturation.

Sensitivity analyses of the surface rate constant on the uptake has been done in Fig. 5 attempting to model the two main natural systems where this process occurs: surface seawater and sea-salt aerosols. We have used a typical concentration of gaseous ozone in the marine troposphere (0.03 ppm) and have assumed [O₃]surf is equal to [O₃]inst. Although there may exist significant phase-resistance that lowers [O₃]surf with respect to [O₃]inst, at such low O₃ concentrations the uptake coefficient due to surface reaction scarcely depends on the ozone concentration (see equation 15), while the uptake coefficient due to the aqueous-phase reaction uptake never depends on the ozone concentration (see equation 9).

We have not taken into consideration a possible variation of the surface propensity of iodide (and thus parameters kₑ and cmax) that could take place when other substances typical in seawater and sea-salt aerosols are present because their influence is not known. These substances include other salts, water-soluble organics, and water-insoluble organics.⁵¹ In addition, sea-salt aerosols and the seawater surface have been observed to be coated by an organic layer which is thought to consist mainly of insoluble saturated species, such as C₁₄-C₁₈ fatty acids, which upon reaction with OH may acquire oxygen moieties.⁵²-⁵⁶ Sodium chloride and other salts may enhance iodide’s
propensity for the surface, but the influence of organics on the surface propensity of iodide is difficult to assess because it has not been sufficiently studied, and because it may depend on the particular kind of organic compounds. The observed lack of inhibition of the surface reaction O3+I− by several organics possessing a short carbon skeleton (≤C6), suggests that some species do not influence the surface propensity of iodide. In contrast, a photoelectron spectroscopic study found that tert-butanol significantly inhibited the surface propensity of iodide, but the concentration of aqueous iodide used in that study was close to saturation and the suppression effect may not necessarily prevail at lower iodide concentrations, for which less iodide competes for surface coverage.

Figure 4. Sensitivity analysis of the maximum surface concentration of iodide ([Cmax]) (a) and the adsorption equilibrium constant of iodide (K) for [O3]eq=1 ppb and [I]=5×10−3 mol L−1 (b), respectively, assuming k=5×10−13 cm3 molecule−1 s−1.

In a study that also used high iodide concentration, O3 uptake by KI iodide particles coated with fatty acids (C9−C30) was found to be lower than in the absence of these surfactants, especially for >C18. However, this decrease was attributed to a hindrance by these organic species to O3 transfer, which is reflected in decreased accommodation coefficients. In that study, the bulk accommodation coefficient of ozone for aerosols containing 7 M KI and saturated fatty acids C18 or C30 were determined to be (3−7)×10−4 and to be much lower than in the absence of an organic coating. Other studies have also found that gas uptake from particles is inhibited to some extent by organic surfactants. However, at atmospherically relevant iodide concentrations the bulk and surface accommodation coefficients of O3 scarcely influence the uptake produced by reaction with iodide because uptake is limited by chemical reaction at these low concentrations, as Rueviere and coworkers noted (see section S2 in the Supplementary Information). In addition, the surface accommodation might not decrease as much as the bulk accommodation coefficient in the presence of surfactants. However, even if the surface accommodation coefficient was as low as 3×10−4 instead of the base case value (1) the total uptake would only be reduced by a factor lower than 2 at <10−4 mol L−1 of iodide.

The adsorption equilibrium constant of O3 has been assumed to be 1×10−15 cm3 molecule−1 for both aerosols and seawater because this is an intermediate value predicted for particles containing organic surfactants, such as stearic acid (C18), octanol, and chlorophyle. Although the high content of NaCl present in seawater and sea-salt aerosols could result in a higher adsorption equilibrium constant, several studies indicate that the effect of organic surfactants may be more important. However, this conclusion and the determined adsorption equilibrium constants may not be valid for a wider range of systems than the ones that have been studied. The uncertainty of the adsorption equilibrium constant leads to a proportional uncertainty in the uptake coefficient for the case of surface reaction dominance, as it can be inferred from Fig. 4b. For example, if the adsorption equilibrium constant of O3 for a particular system was 4×10−14 cm3 molecule−1, as it has been determined to be for oleate, then the uptake due to surface reaction would be 40 times higher than for the base case value assumed. However, oleate is not expected to be found in aerosols and seawater because oleic acid and other fatty acids have high pK values.

Figure 5a shows the predicted uptake coefficient resulting from the interaction of O3 with I− for the usual range of I− concentrations present in surface seawater. A solubility of O3 of 0.24 has been calculated using the Weisenberger-Schumpe and equation and assuming a NaCl concentration of 0.5 mol L−1. As Figure 5a shows, the rate constant of the surface reaction (k) would need to be about 100 times greater than the estimated lower limit given above in order for the surface reaction to contribute to O3 uptake in surface seawater. Because Carpenter et al. have found aqueous-phase kinetics prevail for these conditions, we conclude that k is probably <100 times the lower limit given above. Thus, k=5×10−11 cm3 molecule−1 s−1. For this estimation, we have taken into account unstirred experiments made by Carpenter et al. but we have not used the results of their stirred experiments because stirring probably alters the local concentration of reactants. In fact, Carpenter et al.
inferred possible surface saturation in some unstirred experiments but they did not infer it in any of the stirred ones. However, throughout this work we use the term “surface” to denote the uppermost molecular layer of iodide ions along with adsorbed O₃ because this region is where a Langmuir-Hinshelwood reaction can take place. The thickness of this region is therefore in the order of nanometers (>0.36 nm) and is independent of the concentration of iodide.

Figure Sb shows that predicted contributions of O₃ uptake by sea-salt aerosols are very different from those predicted for surface seawater. A wider interval of iodide concentrations has been studied for this case because field measurements suggest that aerosols may become either depleted or enriched in iodide. The O₃ solubility has been estimated to be 3·10⁻³ using the Weisenger-Schumpe equation 17, 38 based on an assumed NaCl concentration of 5 mol L⁻¹. As the comparison of Figures 5a and Sb reveals, ozone uptake due to the aqueous-phase reaction is two orders of magnitude higher in seawater than in aerosols. This is caused by the high ionic strength of aerosols, which is a result of their drying by air and leads to a low ozone solubility. The fact that salting-out effects on ozone solubility are often overlooked may contribute to understand why the concentrations measured in aerosols are underestimated by current models. However, additional reaction pathways that regenerate I⁻ from more oxidized species, such as HOI, which is taken up from the gas phase, 3, 65 or highly stable iodate (IO₃⁻), 12 are also necessary to explain them. Nonetheless, the high iodide concentrations measured in aerosols have been speculated to possibly derive from an interference by organic compounds in the analysis method. 12

According to Figure Sb the surface reaction could contribute significantly to O₃ uptake by sea-salt aerosols, especially if aerosols are significantly enhanced in iodide with respect to seawater. However, as it was mentioned before, the presence of other species in marine aerosols must be taken into account to accurately model O₃ uptake. In particular, organic species are likely to play an important role in either increasing 31 or inhibiting 38 O₃ uptake. While increased uptake has been linked specifically to acid organic surfactants, 31 additional effects that have been suggested to be caused by organic species include enhancing the solubility of I₂, increasing the particle viscosity, acting as a barrier to gas release, suppressing the surface propensity of iodide, and initiating photochemistry. 19, 23, 35, 57, 58, 66, 67

3. Conclusions

Equations for the uptake coefficient of ozone for its interaction with I⁻(aq) have been obtained using several data from literature to estimate unknown parameters, allowing to illustrate that studies that inferred I⁻(aq) and O₃ react in the aqueous phase do
not contradict studies that inferred that these species react on the surface. The conditions used in each study, mainly \( [O_3]_{aq} \) and \( [I]_{aq} \), but also operating conditions which influence gas-phase resistance and thus \( [O_3]_{aq} \), determine which reaction pathway is dominant. At low \( I \) concentrations, the aqueous-phase reaction dominates because dissolved \( O_3 \) can diffuse through a great depth of the aqueous phase. At high \( [I]_{aq} \) concentrations and sufficiently low \( [O_3]_{aq} \), although not necessarily low \( [O_3]_{aq} \) if gas-phase resistance is limiting, the surface reaction dominates, because solvated \( O_3 \) diffuses only through a shallow area of the aqueous phase due to fast consumption by reaction. At high \( [I] \) and high \( [O_3]_{aq} \), the aqueous phase reaction dominates again due to surface saturation of \( O_3 \).

Based on the concentration of \( I([aq]) \) used in studies of the aqueous phase reaction \( I+O_3 \) and on the analysis of the contribution of the surface and aqueous reaction pathways among \( I([aq]) \) and \( O_3 \) under different conditions, the most reliable determination of the rate constant of the aqueous phase reaction at 25 °C is expected to be \( 2 \times 10^8 \text{L mol}^{-1} \text{s}^{-1} \). For the surface reaction among \( I([aq]) \) and \( O_3 \) we have obtained, by estimating several parameters and constraining the resistor model with results of previous studies of the reaction, a \( 22 \times 10^{13} \text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}. \) Unlike in surface seawater, the surface reaction may significantly influence \( O_3 \) uptake by sea-salt aerosols and their iodine speciation, but the influence of organics and other species present in these aerosols as well as sunlight needs to be studied to model \( O_3 \) uptake accurately.

**Conflicts of interest**

There are no conflicts to declare.

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