

## Supplementary Electronic Information

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

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### S.1 Model for the interaction of ozone with aqueous KI aerosols

#### S.1.1 Aqueous-phase reactions

The list of aqueous-phase reactions that follow if IO<sup>-</sup> or HOI is formed by the reaction of ozone with I<sup>-</sup> is shown in Table 2 from the main text. If the surface reaction of O<sub>3</sub> with I<sup>-</sup> forms a radical, such as I or I<sub>2</sub><sup>-</sup>, as it is concluded to occur in the present work, radical reactions must be included. The reactions involving radical iodinated and oxygen species are shown in Table 3 from the main text and Table S1. In addition, gas-phase reactions involving radical species are shown in Table S2.

**Table S1.** Aqueous-phase radical reactions of oxygen species and follow-up reactions. Based on Gonzalez and Martire<sup>1</sup>.

Reaction number	Reaction	Rate or equilibrium constant
P1	$O_3 + OH^- \rightarrow HO_2^- + O_2$	$k_{P1} = 48 \text{ M}^{-1} \text{ s}^{-1}$
P2	$O_3 + HO_2^- \rightarrow OH + O_2^- + O_2$	$k_{P2} = 5.3 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$
P3	$O_2^- + O_3 \rightarrow O_2 + O_3^-$	$k_{P3} = 1.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$
P4	$O_3^- \leftrightarrow O^- + O_2$	$k_{P4} = 3.5 \cdot 10^3 \text{ s}^{-1}$ $k_{-P4} = 2.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$
P5	$O^- + H_2O \leftrightarrow OH + OH^-$	$k_{P5} = 1.8 \cdot 10^6 \text{ s}^{-1}$ $k_{-P5} = 1.3 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$
P6	$O^- + HO_2^- \rightarrow O_2^- + OH^-$	$k_{P6} = 5.0 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$
P7	$2 O^- + H_2O \rightarrow HO_2^- + OH^-$	$k_{P7} = 1 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$
P8	$O^- + O_2^- + H_2O \rightarrow O_2 + 2 OH^-$	$k_{P8} = 1.8 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$
P9	$2 O_2^- + H_2O \rightarrow HO_2^- + OH^- + O_2$	$k_{P9} < 30 \text{ M}^{-1} \text{ s}^{-1}$
P10	$O_2^- + HO_2^- \rightarrow O^- + OH^- + O_2$	$k_{P10} = 10 \text{ M}^{-1} \text{ s}^{-1}$
P11	$O_3^- + O_2^- (+ H_2O) \rightarrow 2 OH^- + 2 O_2$	$k_{P11} = 5 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$
P12	$O_3 + O^- \rightarrow O_2^- + O_2$	$k_{P12} = 1 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$
P13	$O_3^- + O^- \rightarrow 2 O_2^-$	$k_{P13} = 9 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$

**Table S2.** Gas-phase reactions. Based on Sommariva et al.<sup>2</sup>.

Reaction number	Reaction	Rate constant	Reference
G1	$2 IO \rightarrow I + OIO$	$k_{G1} = 2.4 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Atkinson et al. <sup>3</sup>

G2	$2 \text{ IO} \rightarrow \text{I}_2\text{O}_2$	$k_{\text{G2}}= 3.6 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Atkinson et al. <sup>3</sup>
G3	$\text{I} + \text{O}_3 \rightarrow \text{IO} + \text{O}_2$	$k_{\text{G3}}= 7.7 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Atkinson et al. <sup>3</sup>
G4	$2 \text{ I} \rightarrow \text{I}_2$	$k_{\text{G4}}= 1.8 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Jenkin et al. <sup>4(a)</sup>
G5	$\text{I} + \text{IO} \rightarrow \text{I}_2\text{O}$	$k_{\text{G5}}= 1.0 \cdot 10^{11} \text{ M}^{-1} \text{ s}^{-1}$	Bloss et al. <sup>5</sup>
G6	$\text{I} + \text{I}_2\text{O} \rightarrow \text{IO} + \text{I}_2$	$k_{\text{G6}}= 1.3 \cdot 10^{11} \text{ M}^{-1} \text{ s}^{-1}$	Bloss et al. <sup>5</sup>
G7	$\text{IO} + \text{OIO} \rightarrow \text{I}_2\text{O}_3$	$k_{\text{G17}}= 6.0 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Gomez Martin et al. <sup>6(a)</sup>
G8	$2 \text{ OIO} \rightarrow \text{I}_2\text{O}_4$	$k_{\text{G8}}= 3.0 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Gomez Martin et al. <sup>6</sup>
G9	$\text{I}_2\text{O}_2 \rightarrow 2 \text{ IO}$	$k_{\text{G9}}= 4.0 \cdot 10^{-2} \text{ s}^{-1}$	Ordoñez et al. <sup>7(a)</sup>
G10	$\text{I}_2\text{O}_2 \rightarrow \text{I} + \text{OIO}$	$k_{\text{G10}}= 10 \text{ s}^{-1}$	Ordoñez et al. <sup>7(a)</sup>
G11	$\text{I}_2\text{O}_2 + \text{O}_3 \rightarrow \text{I}_2\text{O}_3 + \text{O}_2$	$k_{\text{G11}}= 6.0 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Saunders and Plane <sup>8(b)</sup>
G12	$\text{I}_2\text{O}_3 + \text{O}_3 \rightarrow \text{I}_2\text{O}_4 + \text{O}_2$	$k_{\text{G12}}= 6.0 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Saunders and Plane <sup>8(b)</sup>
G13	$\text{IO} + \text{O}_3 \rightarrow \text{OIO} + \text{O}_2$	$k_{\text{G13}}= 2.2 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$	Dillon et al. <sup>9</sup>
G14	$\text{I}_2\text{O}_4 \rightarrow 2 \text{ OIO}$	$k_{\text{G14}}= 3.8 \cdot 10^{-2} \text{ s}^{-1}$	Kaltsyannis and Plane <sup>10(a)</sup>

<sup>a</sup>These reactions are accelerated by M (N<sub>2</sub> or O<sub>2</sub>).

<sup>b</sup>These rate constants are estimations instead of determinations.

Although there are more aqueous-phase reactions with known rate constants that could be included in the model, such as the disproportionation of HOI<sup>11</sup>, only the reactions that occur to a significant extent in the system presently studied have been studied. In the present system, aerosols soon become highly alkaline and ozone-aerosol interaction time is in the order of tens of seconds. For example, reactions such as HOI + IO<sup>-</sup> and I<sub>2</sub>OH<sup>-</sup> + IO<sup>-</sup>, with reported kinetic constants of 15 M<sup>-1</sup> s<sup>-1</sup> and 45-2800 M<sup>-1</sup> s<sup>-1</sup>,<sup>12-14</sup> respectively, scarcely have an effect on model results and have not been included.

The kinetic rate constant of reaction R3 has been assumed to be near diffusion control. For reactions R5-R7 involving I<sub>2</sub>OH<sup>-</sup>, the most recent values determined by Buxton and Mulazzani<sup>15</sup> were selected. Among the values that have been reported for the kinetic constant of reaction R11,<sup>13, 16, 17</sup> the one determined by Wren et al.<sup>16</sup> was chosen for the present study because of the similar pH conditions used, which guarantee that I<sub>2</sub>O<sup>2-</sup> and not its protonated form I<sub>2</sub>OH<sup>-</sup> (pK<sub>a</sub>=11.3)<sup>15</sup> is the species dominantly present in their study. The kinetic rate constants of reactions R12 and R15 have not been directly determined previously. Instead, their values have been estimated by Wren et al.<sup>16</sup> to be moderately higher than  $k_9$  and  $k_{11}$  based on the little accumulation of IO<sub>2</sub><sup>-</sup>. With respect to the equilibrium constant  $K_{16}$  for the ionization of water, we have used the generally assumed value of 10<sup>14</sup> M<sup>2</sup> corresponding to pure water at ambient temperature. Although  $K_{16}$  has been determined to be near 10<sup>15</sup> M<sup>2</sup> in an aqueous solution containing 7 M KI,<sup>18</sup> its value may be different in the presence of other salts such as KOH.

Many reactions that are shown in Tables 3 and S1 may not be influential, but they have been included for completeness. The rate constants of the hypothetical radical reactions I<sup>-</sup> + O<sub>3</sub><sup>-</sup>, IO<sup>-</sup> + O<sub>3</sub><sup>-</sup>, and IO<sub>2</sub><sup>-</sup> + O<sub>3</sub><sup>-</sup> are unknown, and have therefore not been included. However, assuming O<sub>3</sub><sup>-</sup> reacts analogously as O<sup>-</sup> and that the decomposition of O<sub>3</sub><sup>-</sup> (P4) is not fast, these reactions are unlikely to be significant considering the rate of reaction P4 (see Table S2). The unknown product of reaction F26 (I<sup>VIII</sup>) is likely to be unstable, but its reactions are not well known.<sup>19</sup> However, the reactions of I<sup>VIII</sup> are not important because this product is estimated to be formed in small concentrations. The reactions of

radical oxygen species (Table S2) have been taken from a source<sup>1</sup> where the reactions were studied using high pH because pH in the present study is high.

### *S.1.2 Transport of volatile species between the gas phase and the aqueous phase of the particle*

According to the reactions shown in Table 2 from the main text, the main gaseous species involved in the aqueous-phase reaction of ozone with I<sup>-</sup> are O<sub>3</sub>, HOI, and I<sub>2</sub>. Modeling O<sub>3</sub> transport is more complex than HOI and I<sub>2</sub> transport because there is a strong radial distribution of the concentration of solvated (aqueous) O<sub>3</sub>. In the present model, O<sub>3</sub> will be assumed to adsorb at the surface layer (O<sub>3(int)</sub>), not to be solvated in the surface layer, to be solvated in the first aqueous phase layer (O<sub>3(aq)</sub>), and not to exist in the second aqueous-phase layer. The assumption that O<sub>3</sub> does not solvate in the surface layer does not introduce an error larger than other uncertainties in the model, such as the exact O<sub>3</sub> solubility near the surface, which is enhanced in I<sup>-</sup> and other ions<sup>20</sup> (see next section). Molecules HOI and I<sub>2</sub> will be assumed to solvate in the surface layer as well as the aqueous-phase layers.

In order to model the transfer of HOI, I<sub>2</sub>, and O<sub>3</sub> from the gas phase into the aqueous phase of the particle, the molar flow of any of these species (generically noted as Y) from the gas phase into the surface layer (HOI, I<sub>2</sub>) or into the first aqueous-phase layer (O<sub>3</sub>) of the aerosols, per gas phase volume ( $F_{g \rightarrow \text{layer}, Y}$ ), was described in the present model by the following equation:

$$F_{g \rightarrow \text{layer}, Y} = k_{g \rightarrow \text{layer}, Y} [Y(g)] \quad (\text{A1})$$

where the subscript “layer” refers either to the aqueous or to surface layer, [Y(g)] is the concentration of Y in the gas phase, and  $k_{g \rightarrow \text{layer}, Y}$  is a transport rate coefficient. The coefficient  $k_{g \rightarrow \text{layer}, Y}$  of each species can be assumed to be proportional to the respective mass accommodation coefficient within small error (0-3%) because gas diffusion of these species is very fast compared to their accommodation due to the low aerosol size, as calculated by the Fuchs and Sutugin<sup>21</sup> approximation (see section S.1.5). The equation relating the mass accommodation coefficient of a species Y and  $k_{g \rightarrow \text{layer}, Y}$  in a flow tube is:<sup>22,</sup>

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$$k_{g \rightarrow \text{layer}, Y} = \frac{\alpha_Y \omega_Y S_p}{4} \quad (\text{S2})$$

where  $\alpha_Y$  is the mass accommodation coefficient of species Y,  $\omega_Y$  is the mean thermal velocity of Y in the gas phase, and  $S_p$  is the particle surface area to gas-phase volume ratio. The accommodation coefficients that have been used for O<sub>3</sub>, HOI, and I<sub>2</sub> are 0.04,<sup>24, 25</sup> 0.1,<sup>26, 27</sup> and 0.02,<sup>28, 29</sup> respectively. The accommodation coefficients of I<sub>2</sub> has been assumed to be the same as that of IBr,<sup>28, 29</sup> respectively, because the former is unknown. Although there is large uncertainty associated to the values of the accommodation coefficients and to  $S_p$ , these values have not been found to influence the model results significantly.

The transfer of volatile species Y in aqueous state from the surface or from the first aqueous layer of the aerosols to the gas phase (process inverse to E2) was described as:

$$F_{\text{layer} \rightarrow \text{g}, \text{Y}} = k_{\text{layer} \rightarrow \text{g}, \text{Y}} [\text{Y}(\text{aq})] \quad (\text{A3})$$

where  $F_{\text{layer} \rightarrow \text{g}, \text{Y}}$  is the molar flow of Y from either the surface layer or the first aqueous layer to the gas phase per surface or first aqueous layer volume, respectively,  $[\text{Y}(\text{aq})]$  is the concentration of Y in the corresponding layer, and  $k_{\text{layer} \rightarrow \text{g}, \text{Y}}$  is a rate coefficient that is calculated using the respective forward transport rate coefficient, the solubility of species Y in the aerosol ( $s_{\text{Y}}$ ), and the gas phase to aerosol layer volume ratio ( $V_{\text{g}}/V_{\text{layer}}$ ) according to the following equation:

$$k_{\text{layer} \rightarrow \text{g}, \text{Y}} = k_{\text{g} \rightarrow \text{layer}, \text{Y}} s_{\text{Y}} \frac{V_{\text{g}}}{V_{\text{layer}}} \quad (\text{A4})$$

The solubility of O<sub>3</sub>, HOI, and I<sub>2</sub> in pure water at room temperature have been determined to be 9.7·10<sup>-3</sup> M atm<sup>-1</sup>,<sup>30</sup> 450 M atm<sup>-1</sup>,<sup>31</sup> and 3 M atm<sup>-1</sup>,<sup>31</sup> respectively. However, the solubility of these species in 7 M KI aerosols reacting with O<sub>3</sub> are expected to be different than in pure water due to the high concentrations of dissolved electrolytes (salting-out effect), and are likely to vary with the changing concentration of the salts (mainly KI and KOH).<sup>32</sup> However, the solubilities used for HOI and I<sub>2</sub> in the present study correspond to pure water as solvent because the effect of salts has not been estimated, according to the authors' knowledge.<sup>33</sup> The closest salt to KI whose effect on I<sub>2</sub> solubility has been studied is KCl, which was found to increase the solubility (salting-in), instead of decrease (salting-out).<sup>34</sup> The effect of mixed salts on O<sub>3</sub> solubility will be estimated using the semi-empirical equation of Weisenberger and Schumpe<sup>32</sup>, even though this method is most reliable only up to 1.5 M.<sup>35</sup>

$$s = s_0 \cdot 10^{-\sum(h+h_{\text{ion}}) \cdot c_{\text{ion}}} \quad (\text{A5})$$

where  $s_0$  is the ozone solubility in pure water (expressed in liquid/gas concentration ratio) at a given temperature,  $c_{\text{ion}}$  is the concentration of a particular ion present,  $h_{\text{ion}}$  is the coefficient assigned to this ion,  $h$  is a coefficient specific to the gaseous molecule (O<sub>3</sub>) and depends on temperature, and the summation extends to all dissolved ions that are present. Coefficient  $h$  is 0.073 L mol<sup>-1</sup> at 300 K, and the coefficients  $h_{\text{ion}}$  for the major ions present in 7 M KI aerosols exposed to ozone (K<sup>+</sup>, I<sup>-</sup>, IO<sub>3</sub><sup>-</sup>, and OH<sup>-</sup>) are shown in Table S3.

**Table S3.** Parameter values of the Weisenberger-Schumpe equation for the species involved in the present study. Based on Weisenberger and Schumpe<sup>32</sup>.

Species	$h_{\text{ion}} / \text{M}$
K <sup>+</sup>	0.0922
I <sup>-</sup>	0.0039
IO <sub>3</sub> <sup>-</sup>	0.0913
OH <sup>-</sup>	0.0839

The ozone solubility is predicted to decrease during reaction due to KOH formation, as OH<sup>-</sup> is a stronger salting anion than I<sup>-</sup> (see Table S3). Before exposure to ozone, the aerosols are estimated to have a composition consisting of about 7 M KI (see main text). However, within the reacto-diffusive region, which is only about 0.4 nm deep for this concentration (see equation 2 in main text), the composition is estimated to be about 7 M K<sup>+</sup> + 11 M I<sup>-</sup>.<sup>25</sup> As I<sup>-</sup> becomes converted, the reacto-diffusive length increases and the ozone solubility decreases because I<sup>-</sup> is replaced mostly by OH<sup>-</sup>. The minimum ozone solubility is estimated to be reached for a composition of 7 M KOH. However, for this composition, ozone solubility is not very relevant because I<sup>-</sup> has already become consumed. Therefore, the representative ozone solubility value will be estimated as the sum of 70% the ozone solubility for 7 M K<sup>+</sup> + 11 M I<sup>-</sup> and 30% the ozone solubility for 7 M KOH (see Table S4).

**Table S4.** Aerosol compositions considered to estimate approximate ozone solubility in aerosols throughout reaction time. The representative value is taken to be the intermediate value of  $1.2 \cdot 10^{-3}$  M atm<sup>-1</sup> (see text).

Composition	Ozone solubility / $10^{-3}$ M atm <sup>-1</sup>
7 M K <sup>+</sup> + 11 M I <sup>-</sup>	1.5
7 M KOH	0.45

For 7 M KI aerosols, ozone becomes consumed in the aqueous phase within a short depth (about 0.4 nm) (see equation 2 in the main text). For this reason, O<sub>3</sub> is assumed not to solvate in the second aqueous layer, which is the largest. Furthermore, the low extent of O<sub>3</sub> diffusion throughout the particle depth will be accounted for by assuming a fictitious lower solubility in the first aqueous layer that is obtained by multiplying the estimated solubility by the O<sub>3</sub> moles actually present in the particle ( $n_{O_3}$ ), and dividing it by the O<sub>3</sub> moles that would be present if there was no resistance to ozone diffusion and/or no chemical reaction ( $n_{O_3, \text{fict}}$ ). The number of O<sub>3</sub> moles present in the particle are calculated considering the radial distribution of the aqueous O<sub>3</sub> concentration ( $[O_3]_{\text{aq}}$ ) and integrating this concentration over the particle volume:

$$n_{O_3} = \int^V [O_3]_{\text{aq}} dV = \int^V [O_3]_{\text{aq, max}} \cdot \exp\left(-\frac{r_p - r}{l}\right) dV = \int_0^{r_p} [O_3]_{\text{aq, 0}} \cdot \exp\left(-\frac{r_p - r}{l}\right) 4\pi r^2 dr$$

(A6)

where  $V$  is the particle volume,  $[O_3]_{\text{aq, max}}$  is the concentration of aqueous ozone determined by the ozone solubility in the case of no reaction and/or no resistance to diffusion,  $l$  is the reacto-diffusive length (see equation 2 from the main text),  $r_p$  is the particle radius, which is about the same as the radius of the first aqueous layer, and  $r$  is the distance of a point within the particle to the center of the particle.

The solution of the integral given above is as follows:

$$n_{O_3} = [O_3]_{\text{aq, max}} \cdot 4\pi \cdot \exp\left(-\frac{r_p}{l}\right) \cdot \left\{ r_p^2 l \cdot \exp\left(\frac{r_p}{l}\right) - 2l^2 r_p \exp\left(\frac{r_p}{l}\right) + 2l^3 \exp\left(\frac{r_p}{l}\right) - 2l^3 \right\}$$

(A7)

Parameter  $n_{O_3, \text{fict}}$  is deduced using geometric considerations:

$$n_{O_3, \text{fict}} = [O_3]_{\text{aq, max}} \cdot \frac{4}{3} \pi (r_2^3 - r_3^3) \quad (\text{A8})$$

Dividing the previous two equation, the following equality is obtained:

$$\frac{n_{O_3}}{n_{O_3, \text{fict}}} = \frac{3 \exp\left(\frac{-r_p}{l}\right)}{(r_2^3 - r_3^3)} \left\{ r_p^2 l \exp\left(\frac{r_p}{l}\right) - 2l^2 r_p \exp\left(\frac{r_p}{l}\right) + 2l^3 \exp\left(\frac{r_p}{l}\right) - 2l^3 \right\} \quad (\text{A9})$$

The aqueous-phase diffusion coefficient of  $O_3$  ( $D_{\text{aq}, O_3}$ ) influences the rate of  $O_3$  diffusion with a square-root relation. It is therefore less influential than the  $O_3$  solubility and using the value for pure water as solvent may be justified. The error of this assumption is estimated to be small because the presence of KI does not influence the viscosity of aqueous solutions much.<sup>36</sup> For example, for a 3 M KI solution, the diffusion coefficient of gaseous molecules is estimated to increase by 9% with respect to pure water;<sup>25, 36</sup> therefore, the uptake coefficient due to aqueous phase reaction in this solution is estimated to decrease by only 4.5%.

If radicals are formed by the surface reaction of ozone with I, as it is hypothesized in the main text, the following radical volatile species might be formed: I, IO, OIO,  $I_2O$ ,  $I_2O_2$ ,  $I_2O_3$ , and  $I_2O_4$ . In addition,  $O_2$  can react with several radical species that may be formed. The accommodation coefficients of these species will be assumed to be the same as the one used for HOI (0.1), as these coefficients scarcely have any influence. The reported or estimated solubilities of all these species in pure water are indicated in Table S5. The values indicated in this table will be used even though most of them are arbitrary estimations because, according to the authors' knowledge, there are no available estimations of these parameters.

**Table S5.** Solubilities of radical iodinated species, as reported in other works or estimated in the present work.

Species	Solubility / M atm <sup>-1</sup>	Reference or note
$O_2$	$1.9 \cdot 10^{-4}$	Weisenberger and Schumpe <sup>32a</sup>
I	$8.1 \cdot 10^{-3}$	Schwarz and Bielski <sup>37</sup> , Mozurkewich <sup>38</sup>
IO	$4.5 \cdot 10^2$	Note <sup>b</sup>
$I_2O$	30	Note <sup>c</sup>
OIO	$4.5 \cdot 10^3$	Note <sup>d</sup>
$I_2O_2, I_2O_3, I_2O_4$	300	Note <sup>e</sup>

<sup>a</sup>This value is an average weighted as 70% the value for 7 M KI M and 30% the value for 7 M KOH. The explanation is the same as for the ozone solubility (see text).

<sup>b</sup>Assumed to be the same as for HOI.

<sup>c</sup>Assumed to be 10 times higher than for  $I_2$ .

<sup>d</sup>Assumed to be 10 times higher than for IO.

<sup>e</sup>Assumed to be 100 times higher than for  $I_2$ .

### S.1.3 Transport of species between aqueous layers

The model includes an estimation of the propensity of some of the most abundant anionic iodinated species ( $I^-$ ,  $IO^-$ ,  $IO_2^-$ ,  $I_3^-$ ,  $IO_3^-$ ) for the air-aqueous interface. The relation between  $[I^-]_{\text{surf}}$  and  $[I^-]_{\text{aq}}$  has been estimated previously, but with much uncertainty.<sup>25</sup> This estimation is most uncertain for low  $I^-$  concentrations, which are not relevant in the present work. For concentrations near 3 M,  $[I^-]_{\text{surf}}$  is known to be 3.5 times higher than  $[I^-]_{\text{aq}}$ .<sup>39</sup> In the present work, it will be assumed that the concentration ratio  $[I^-]_{\text{surf}}/[I^-]_{\text{aq}}$  for all iodide concentrations is 2 for simplicity. This assumption has some influence on model results, as shown in Figure S1, where  $I^-$  consumption and  $I^-$  conversion to  $IO_3^-$  in deliquesced KI aerosols exposed to ozone have been plotted assuming different ratios of  $[I^-]_{\text{surf}}/[I^-]_{\text{aq}}$  (1 and 2) (compare with Figure 4 from the main text). However, a proper estimation of the ratio for the iodide concentrations relevant in the present work (0.5-7 M) and for the surface depth relevant in the present work (the iodide diameter) cannot be made with currently available data (see further discussion in the main text).

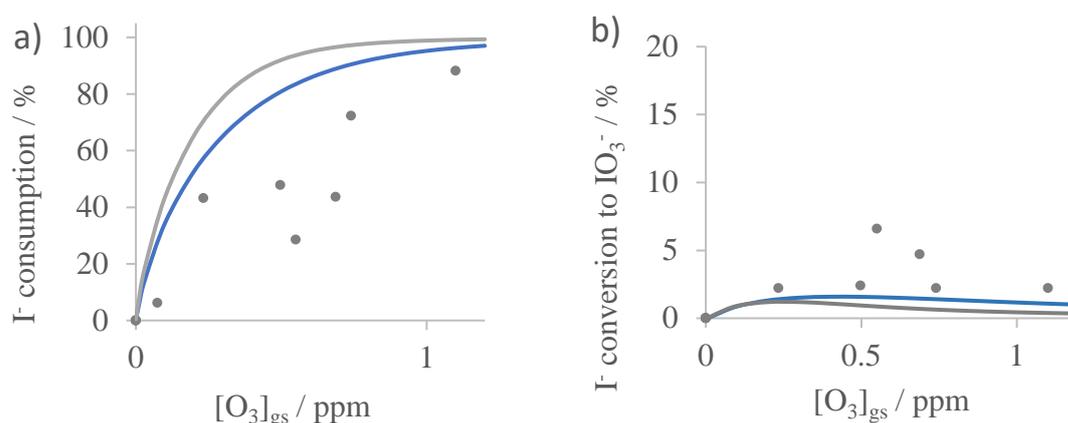


Figure S1. Model-predicted consumption of iodide (a) and iodide conversion to iodate (b) in deliquesced KI aerosols exposed to ozone using the operation parameters shown in Table 1, combination of reactions C from Table 6, and different assumptions of the value  $[I^-]_{\text{surf}}/[I^-]_{\text{aq}}$ : 1 (gray lines) and 2 (blue lines). Dots represent experimental data.

The  $[ion]_{\text{surf}}/[ion]_{\text{aq}}$  ratio, which will be referred as  $A_{\text{ion}}$ , for the other ions present in the aerosols are not known. Iodate ( $IO_3^-$ ), a kosmotrope, is believed not to have surface propensity,<sup>40, 41</sup> while  $OH^-$  is believed to have surface propensity but to reside below the outermost layer of the surface.<sup>42, 43</sup> For simplicity,  $A_{\text{ion}}$  will be assumed to be 1 for  $IO_3^-$  and for  $OH^-$ . By contrast, the ions  $IO^-$ ,  $IO_2^-$ , and  $I_3^-$  are expected to have significant surface propensity because they have a larger size than  $I^-$ .<sup>41, 44, 45</sup> For ions that are estimated to be present in very low concentrations ( $IO_2^-$  and  $I_3^-$ ),  $A_{\text{ion}}$  has been assumed to be 10 in the present work because the  $[I^-]_{\text{surf}}/[I^-]_{\text{aq}}$  ratio is estimated to be very high (about 40) at low  $I^-$  concentrations ( $<0.1$  M).<sup>25</sup> For  $IO^-$ , which is estimated to be present in moderate concentrations (about 0.5 M),  $A_{\text{IO}^-}$  assumed to be the intermediate value of 5. Selected values of  $A_{\text{ion}}$  for the main ions involved

in the present interaction are compiled in Table S6. Although these ratios have been estimated quite arbitrarily, they do not have much influence on model results. Ions not shown in Table A6 are assumed to have neutral propensity for the surface ( $A_{\text{ion}}=1$ ).

**Table S6.** Estimated values of parameter  $A_{\text{ion}}$  for the main ions expected to be involved in the interaction of ozone with concentrated KI aerosols.\*

Ion	$A_{\text{ion}}$
I <sup>-</sup>	2
IO <sub>2</sub> <sup>-</sup> , I <sub>3</sub> <sup>-</sup>	10
IO <sup>-</sup>	5
IO <sub>3</sub> <sup>-</sup> , OH <sup>-</sup>	1

\*See the text in this section for definition of  $A_{\text{ion}}$ .

The equation to model the molar flow of a species from a layer to an adjacent layer per aqueous-phase layer volume ( $F_{\text{layer} \rightarrow \text{layer}'}$ ) is the following:

$$F_{\text{layer} \rightarrow \text{layer}'} = k_{\text{layer} \rightarrow \text{layer}'} [\text{species}]_{\text{aq}} \quad (\text{A10})$$

where  $k_{\text{layer} \rightarrow \text{layer}'}$  is a mass transfer coefficient whose value does not necessarily follow Fick's law because the distance between layers in this case is in the order of nanometers.<sup>46, 47</sup> However, since this coefficient is unknown, it will be estimated using Fick's law, which leads to the following equations:<sup>47</sup>

$$k_{\text{aq1} \rightarrow \text{surf}} = \frac{24D_{\text{aq}}}{(\delta_{\text{aq1}} + \delta_{\text{surf}})} \frac{r_{\text{aq1}}^2}{(r_{\text{aq1}}^3 - r_{\text{aq2}}^3)} \quad (\text{A11})$$

$$k_{\text{aq2} \rightarrow \text{aq1}} = \frac{24D_{\text{aq}}}{(r_{\text{aq2}} + \delta_{\text{aq1}})} \frac{1}{r_{\text{aq2}}} \quad (\text{A12})$$

where  $\delta_{\text{surf}}$  and  $\delta_{\text{aq1}}$  are the thickness of the surface and first aqueous layers, respectively, and  $r_{\text{surf}}$ ,  $r_{\text{aq1}}$ , and  $r_{\text{aq2}}$  are the radius of the surface layer and the first and second aqueous layers, respectively. The inverse mass transfer coefficients can be deduced by mass balance considerations:

$$k_{\text{surf} \rightarrow \text{aq1}} = k_{\text{aq1} \rightarrow \text{surf}} \frac{V_{\text{aq1}}}{V_{\text{surf}}} \quad (\text{A13})$$

$$k_{\text{aq1} \rightarrow \text{aq2}} = k_{\text{aq2} \rightarrow \text{aq1}} \frac{V_{\text{aq2}}}{V_{\text{aq1}}} \quad (\text{A14})$$

where  $V_{\text{surf}}$  is the volume of the surface layer and  $V_{\text{aq1}}$  and  $V_{\text{aq2}}$  is the volume of the first and second aqueous layers, respectively. Coefficients  $k_{\text{aq1} \rightarrow \text{surf}}$  and  $k_{\text{aq2} \rightarrow \text{aq1}}$  has a very small influence on model results of I<sup>-</sup> consumption and IO<sub>3</sub><sup>-</sup> formation.

The aqueous-phase diffusion coefficient of all species has been assumed to be equal to that of O<sub>3</sub> for simplicity because, like transport coefficients, all diffusion coefficients of all species apart from O<sub>3</sub> are not influential.

#### S.1.4 Ozone adsorption

The molar flow of ozone adsorbing at the aqueous surface has been modeled as follows:<sup>25</sup>

$$F_{\text{ads}} = k_{\text{ads}}[\text{O}_3]_{\text{gs}}[\text{I}^-]_{\text{surf}} \quad (\text{A15})$$

where  $[\text{O}_3]_{\text{gs}}$  is approximately equal to  $[\text{O}_3]_{\text{g}}$  in the present work (see next section) and  $k_{\text{ads}}$  is the adsorption rate coefficient, which was implicitly proposed in our previous work to be given by the following equation:<sup>25</sup>

$$k_{\text{ads}} = p^{\text{I}^-}[\text{I}^-]_{\text{surf}} \frac{\omega S_{\text{p}}}{4} \quad (\text{A16})$$

where  $p^{\text{I}^-}$  is a constant related to the surface accommodation coefficient whose value has been estimated to be  $0.03 \text{ M}^{-1}$ .<sup>25</sup> The molar flow of ozone desorption has been modeled according to the following equation:

$$F_{\text{d}} = k_{\text{d}}[\text{OOOI}^-]_{\text{surf}} \quad (\text{A17})$$

where  $k_{\text{d}}$  is the desorption rate coefficient, which is given by the following equation:<sup>47</sup>

$$k_{\text{d}} = \frac{k_{\text{ads}}}{K_{\text{O}_3^{\text{I}^-}}} \frac{V_{\text{g}}}{V_{\text{surf}}} \quad (\text{A18})$$

where the value of the adsorption equilibrium constant of ozone on I<sup>-</sup> molecules ( $K_{\text{O}_3^{\text{I}^-}}$ ) at ambient temperature has been indicated in the main text.

#### S.1.5 Gas-phase diffusion

The resistance to diffusion of molecules across the gas phase within a nanoaerosol dispersion is fast compared to mass accommodation, as it can be calculated using the Fuchs and Sutugin<sup>21</sup> approximation. In the present case, assuming a particle diameter of 80 nm, the gas-phase resistance only decreases the rate of molecule transfer from the gas phase into the particle by <3%. As this variation is lower than the uncertainty of the accommodation coefficient, gas-phase resistance does not need to be considered to model gas transport into the aqueous phase in the present case.

According to a previous estimation based on experimental results, the surface accommodation coefficient for a concentrated I<sup>-</sup> solution is about 1.<sup>25</sup> The conductance of gas-phase diffusion is a fraction (0.42) of the value of the conductance of surface accommodation. However, the ratio  $[\text{O}_3]_{\text{gs}}/[\text{O}_3]_{\text{g}}$  for the uptake coefficient value of the aqueous-phase reaction of ozone with I<sup>-</sup> for 7 M KI (about 0.01)<sup>24, 48, 49</sup> and for a Knudsen number of 0.7 is very close to 1,<sup>47</sup> where Kn is the Knudsen number, which is defined as  $3 D_{\text{g}}/(2d_{\text{p}}\omega)$ , where  $D_{\text{g}}$  is the gas-phase diffusion coefficient. In addition,

the rate of gas adsorption is not influential within a factor of 2. Therefore, gas phase resistance does not need to be considered to model gas adsorption either in the present case.

### S.1.6 Sensitivity analysis

As the interaction of ozone with aqueous iodide for 22 s involves many reactions and physical processes, there is a high number of uncertain parameters in the present model, including rate constants, compound solubilities, and accommodation coefficients. A sensitivity analysis of uncertain parameters has been done. Most parameters have no influence (<0.1 %), except for the following ones:

- Solubility of I<sub>2</sub>. If it were 10 times lower, model-predicted I<sup>-</sup> would decrease by 20% and model-predicted IO<sub>3</sub><sup>-</sup> would decrease by 40%.
- I<sub>2</sub> accommodation coefficient. If it were 50 times higher, model-predicted I<sup>-</sup> would be about 20% higher and model-predicted IO<sub>3</sub><sup>-</sup> would not change.
- Rate constant k<sub>F13</sub>. If it were 10 times higher, model-predicted I<sup>-</sup> would be 3% lower and model-predicted IO<sub>3</sub><sup>-</sup> would be 15% lower.
- Rate constant k<sub>15</sub>. If it were 10 times higher, model-predicted I<sup>-</sup> would not change and model-predicted would be 15% lower.
- HOI Accommodation coefficient. If it were 10 times higher, model-predicted I<sup>-</sup> would not change, and model-predicted IO<sub>3</sub><sup>-</sup> would increase by 5%.

In addition, as indicated in the text, the uncertainty in the iodide enhancement in the model's first aqueous layer has the strongest effect on model-predicted values, as it could influence by up to a factor of 3.

## S.2 Determination of the rate constant for the surface reaction of O<sub>3</sub> with solid I<sup>-</sup>

An uptake coefficient of  $(1.4 \pm 0.7) \cdot 10^{-4}$  was determined for the interaction of O<sub>3</sub> with solid KI by Brown et al.<sup>50</sup>, who measured the surficial concentration of IO<sub>3</sub><sup>-</sup> formed upon this interaction for [O<sub>3</sub>]<sub>g</sub>=3·10<sup>-6</sup> ppm and low humid relativity (< 2%) at room temperature. From these data, the surface reaction rate constant ( $k_{\text{solid}}$ ) can be estimated assuming the uptake due to this reaction ( $\gamma_{\text{solid}}$ ) can be explained by the same type of model as the uptake due to the surface reaction at the aqueous surface.<sup>25</sup> This model assumes that O<sub>3</sub> adsorbs on I<sup>-</sup> forming an adduct, which then reacts through a first order reaction. The uptake model is the following one:<sup>25</sup>

$$\frac{1}{\gamma_{\text{solid}}} = \frac{\omega}{4k_{\text{solid}}} \frac{1+K_{\text{O}_3}[\text{O}_3]_{\text{gs}}}{K_{\text{O}_3}} \frac{1}{[\text{I}^-]_{\text{surf}}} \quad (\text{A19})$$

where  $\omega$  is the mean square root velocity ( $\sqrt{8RT/\pi M}$ ),  $K_{O_3}$  is the adsorption equilibrium constant of ozone, and  $[I]_{\text{surf}}$  is the iodide concentration at the surface. The surface accommodation coefficient has been estimated to be 1 for an aqueous surface filled with I,<sup>25</sup> and it will therefore be assumed to be 1 for a solid surface. The value of  $K_{O_3}$  may also be assumed to be the same as for an aqueous surface containing I ( $2 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$  for a temperature of 21 °C).<sup>25</sup> The concentration  $[I]_{\text{surf}}$  on solid KI is expected to be similar to the concentration of  $[IO_3^-]_{\text{surf}}$ , which is  $2.4 \cdot 10^{14} \text{ molecule cm}^{-2}$ .<sup>51</sup> As it is difficult to evaluate the gas-phase resistance for aqueous media different from nanoaerosols, it will be assumed it is zero and, therefore, that  $[O_3]_{\text{gs}}$  is equal to  $[O_3]_{\text{g}}$ . Therefore, the surface reaction rate constant to be determined may be considered a lower limit, whose result is  $>0.25 \text{ s}^{-1}$ .

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