Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

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

Carolina Moreno, Oscar Gálvez, Vicente López-Arza Moreno, Eva María Espildora García, María Teresa Baeza-Romero

S1. Sensitivity analysis of accommodation coefficients on uptake coefficients

Sensitivity analyses of the bulk (α_b) and surface (α_s) accommodation coefficients on uptake coefficients are shown in Fig. S1. For the former, the values α_b=0.01 versus the base case value (α_b=0.1) have been contrasted (Fig. S1a). The minimum value of α_b should be 0.002, as this is the value determined for water,[1] and should prevail at sufficiently low iodide concentrations, while the maximum value is expected to be >0.1 because this is the value determined for 3 mol L^{-1} aqueous NaI particles. For the surface accommodation coefficient, the values that have been contrasted in Fig. S1b are the minimum possible value, which is equal to the bulk accommodation coefficient (α_s=0.1) versus the maximum value (α_s=1). Both Figures S1a and S1b show that both accommodation coefficients influence uptake only at high iodide concentrations (>0.1 mol L^{-1} and >0.01 mol L^{-1}, respectively). This is because at high iodide concentrations the rate of reaction is fast enough so that O_3 uptake can become limited by accommodation instead of reaction.

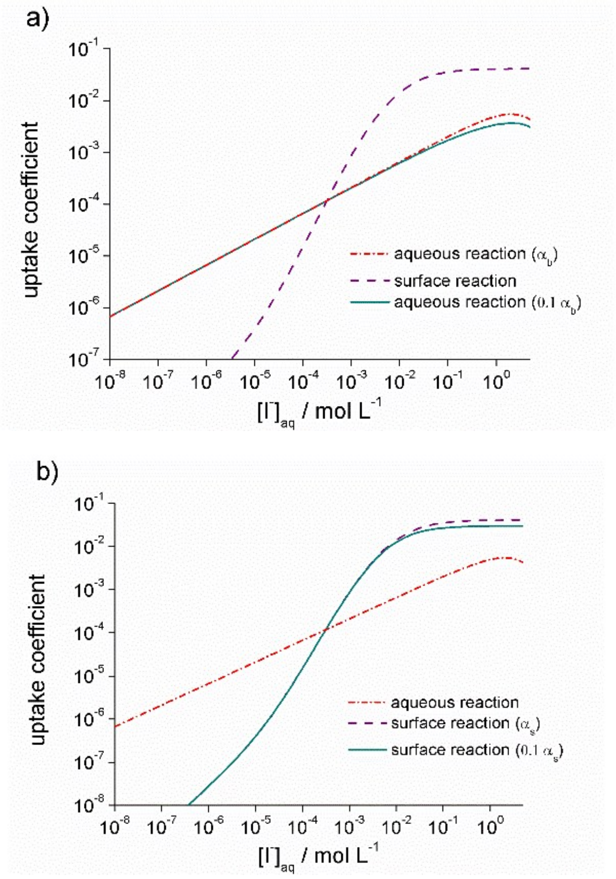

Fig. S1 Sensitivity analysis of the bulk **(a)** and surface **(b)** accommodation coefficient for $[O_3]_{gs}$=1 ppm. The studied value is given between parenthesis as a function of the base case value (α_b and α_s, respectively).

S2. Determination of apparent adsorption constants

Figure 1 in Reeser et al.'s work[2] shows measured I_2 production as a function of O_3 concentration for $[I^-]_{aq}$=0.01 mol L^{-1} and for a particular set of operating conditions (residence time of ozone, reactor dimensions, etc). The data from this figure have been used to obtain the apparent adsorption constant of ozone ($K_{O3,app}$) for those particular conditions, as explained below.

The data from the cited figure have been fit to a linear function that derives from equation 22:

$$[O_3]_g/n_{iodine} = \frac{\sigma}{f \cdot K_{O_{3,app}}} + \frac{\sigma}{f}[O_3]_g$$

where n_{iodine} is the amount of I_2 produced and f is the factor of proportionality between the concentration of adsorbed ozone and I_2 produced by the surface reaction among ozone and iodide. From the above equation it follows that a linear correlation of $[O_3]_g/n_{\text{iodine}}$ versus $1/[O_3]_g$ can be used to obtain $K_{O3,app}$ by dividing the y-intercept by the slope of this linear correlation. Using the slope and y-intercept of the correlation shown in Fig. S2a, the apparent constant for Reeser et al.'s[2] conditions is determined to be $1.9 \cdot 10^{-19}/3.0 \cdot 10^{-4}$ cm^3 $molecule^{-1}$ = $6 \cdot 10^{-16}$ cm^3 $molecule^{-1}$.

The same linearization has been used to obtain the apparent adsorption equilibrium constant for Sakamoto et al.'s[3] results of concentration of gas phase I_2 as a function of ozone concentration (their Figure 3). The correlation is shown in Fig. S2b, whose slope and y-intercept allow to calculate $K_{O3,app}=4 \cdot 10^{-15}$ cm^3 $molecule^{-1}$.

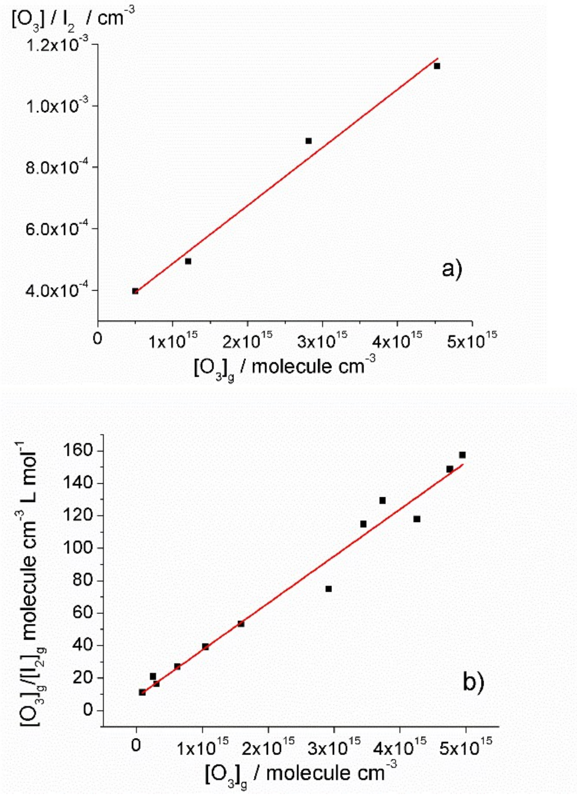

Fig. S2 Linearization of data reported by Reeser et al.[2] for $[I^-]_{aq}$=0.01 mol L^{-1} **(a)** and by Sakamoto et al.[3] for $[I^-]_{aq}=5 \cdot 10^{-3}$ mol L^{-1} **(b)** to obtain apparent adsorption equilibrium constants of ozone.

S3. Estimation of the rate constant of the surface reaction $I^-_{(int)}+O_{3(surf)}$

Minimum and maximum rate constants (k_s) of the surface reaction $I^-_{(int)} + O_{3(surf)}$, where $I^-_{(int)}$ is aqueous iodide residing at the surface and $O_{3(surf)}$ is adsorbed ozone, have been estimated using results from literature as explained below.

A lower limit of the rate constant can be estimated using the concentrations of a study where the surface reaction was found to be dominant and where the concentration of gaseous ozone near the surface ($O_{3(gs)}$) was relatively high, as sufficiently high concentrations of $O_{3(gs)}$ lead to aqueous-phase reaction dominance due to surface saturation in ozone. Results shown in Figure 3 by Sakamoto et al.[3] meet these conditions, where maximum $[O_3]_{gs}$ is believed to be 17 ppm (see section S2) and $[I^-]_{aq}=5\cdot10^{-3}$ mol L^{-1}. The lower limit of k_s has been estimated imposing as a condition that, for these reactant concentrations, the uptake due to surface reaction be equal to the uptake to the aqueous-phase reaction. The result is $k_{s,min}=3\cdot10^{-13}$ cm^2 molécule^{-1} s^{-1}. Figure S3a shows the predicted uptakes for each reaction pathway for the conditions used by Sakamoto et al.[3]

An upper limit of the surface reaction rate constant can be estimated by considering the conditions of a study where a relatively high concentration of iodide and a low ozone concentration were used and aqueous-phase reaction dominance was concluded, as sufficiently high iodide concentrations lead to surface reaction dominance, according to the present model. Therefore, the conditions of the results of Carpenter et al.[4] will be used (specifically, their experiments with pure KI solution from Figure 1c). These authors[4] used an iodide concentration of up to $5\cdot10^{-5}$ mol L^{-1} and $[O_3]_g=0.15$ ppm. In this case, it is not necessary to estimate $[O_3]_{gs}$ to calculate the uptake because the uptake scarcely depends on $[O_3]_{gs}$ at concentrations as low as 0.15 ppm. Imposing as a condition that, for these concentrations, the uptake coefficient due to each reaction pathway be equal to each other, a maximum surface reaction rate constant of $4\cdot10^{-12}$ cm^2 molecule^{-1} s^{-1} is obtained. Figure S3b shows the predicted uptake coefficients for the conditions used by Carpenter et al.[4]

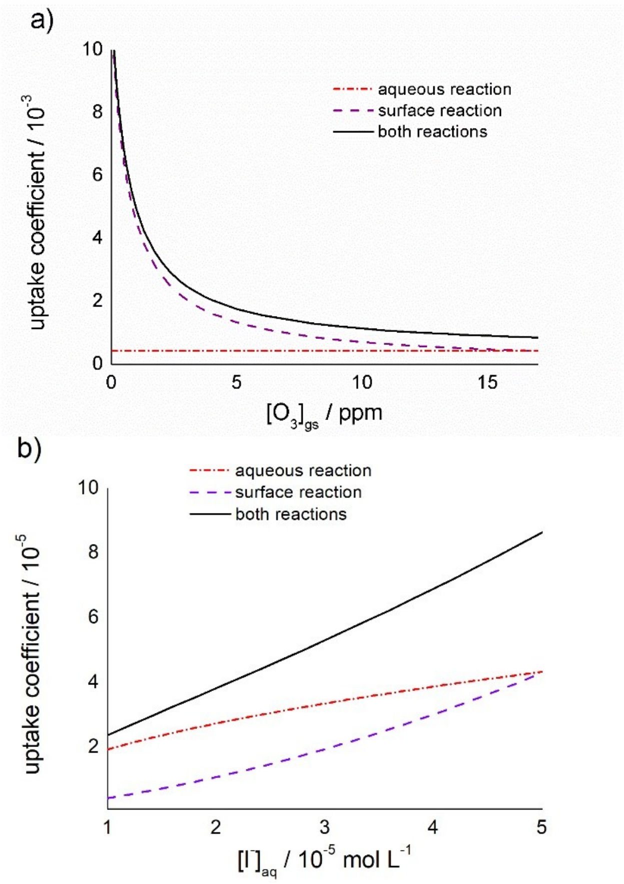

Fig. S3 Predicted uptake coefficients under the conditions used to estimate the lower and upper limit of the surface reaction rate constant (k_s), respectively. Figure **a** corresponds to Sakamoto et al.'s[3] conditions (their Figure 3), where

$[I^-]_{aq}=5\cdot10^{-3}$ mol L^{-1}, and to the lower limit of k_s presently estimated, and Figure **b** corresponds to Carpenter et al.'s conditions[4] (their Figure 1c), where $[O_3]_{gs}<0.15$ ppm, and to the upper limit of k_s estimated in the present work.

References

1. R. G. Utter, J. B. Burkholder, C. J. Howard and A. R. Ravishankara, *The Journal of Physical Chemistry*, 1992, 96, 4973-4979.
2. D. I. Reeser and D. J. Donaldson, *Atmos. Environ.*, 2011, 45, 6116-6120.
3. Y. Sakamoto, A. Yabushita, M. Kawasaki and S. Enami, *J. Phys. Chem. A*, 2009, 113, 7707-7713.
4. L. J. Carpenter, S. M. MacDonald, M. D. Shaw, R. Kumar, R. W. Saunders, R. Parthipan, J. Wilson and J. M. C. Plane, *Nature Geosci.*, 2013, 6, 108-111.