

**IUPAC Subcommittee on Gas Kinetic Data Evaluation –  
Data Sheet VI.A2.0 HET\_SALTS\_0**

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**O<sub>3</sub> + Cl<sup>-</sup>/Br<sup>-</sup>/I<sup>-</sup> (aq) → products**

**Experimental data**

<i>Parameter</i>	Temp./K	<i>Reference</i>	<i>Technique/ Comments</i>
<i>Uptake, Accommodation coefficients: <math>\gamma</math>, <math>\alpha</math></i>			
$\gamma_{ss} > 2 \times 10^{-3}$ ( $\pm 20\%$ ) (SnCl <sub>2</sub> solution)	276	Utter et al., 1992	WWFT (a)
$\alpha_b = 0.10$ $1/\gamma_1 = (85^{+20}_{-10})a(I^-)^{-1/2} + (10 \pm 5)$ with [I <sup>-</sup> ] between 0.5 and 3.0 M	277	Hu et al., 1995	DT-MS (b)
$\gamma_{ss} = 3.7 \times 10^{-3}$ ( $a(I^-) = 0.36$ M)	282	Magi et al., 1997	DT-MS (c)
$\gamma_{ss} = 1.16 \times 10^{-2}$ ( $a(I^-) = 2.89$ M)	282		
$\gamma_{SS} < 1.0 \times 10^{-4}$ (unbuffered and buffered (pH = 7.2) NaCl aerosol)	300	Abbatt and Waschewsky, 1998	AFT-CIMS (d)
$\alpha_b > 2.0 \times 10^{-2}$ (NaI solution)	298	Schütze and Herrmann, 2002	(e)
$\alpha_b = 0.6 \pm 0.4_{0.5}$ (deliquesced KI aerosol, rh = 72%)	293	Rouvière et al., 2010	AFT (f)
$\gamma_0 = (1.1 \pm 0.2) \times 10^{-2}$ (excess I <sup>-</sup> )			
$\gamma_0 = 4.4 \times 10^{-4}$ (mixed KI/NaCl aerosol with [I <sup>-</sup> ] = 0.9M, [Cl <sup>-</sup> ] = 6.1M)			
$1/\gamma_s = (1.4 \pm 0.2) \times 10^{-7}[O_3] + 0.06 \times 10^7$	273	Oldridge and Abbatt, 2011	CWFT (g)
$\gamma_1 = (7.7 \pm 1.8) \times 10^{-8}$	273		

**Comments**

- (a) Uptake of O<sub>3</sub> (10<sup>11</sup> molecule cm<sup>-3</sup>) to a liquid film (20 μm thick). The total pressure was between 13.6 to 14.6 mbar with half of it being H<sub>2</sub>O vapor. No uptake of O<sub>3</sub> was observed into pure deionized water, but  $\gamma$  increased as a function of the concentration of the trapping agent (*e.g.*, SnCl<sub>2</sub>) to values in the 10<sup>-2</sup> range. The measured loss rate was limited by the diffusion of O<sub>3</sub> to the wetted wall when  $\gamma$  was larger than 0.02 in the presence of solutions of scavengers Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and SnCl<sub>2</sub>.
- (b) Droplet diameters in the range 120-250 μm. The concentration of O<sub>3</sub> varied from 5 × 10<sup>12</sup> to 1 × 10<sup>14</sup> molecule cm<sup>-3</sup> at a gas residence time between 2 to 15 ms. Detection of the reactant gas is by residual gas electron-impact quadrupole mass spectrometry. The partial pressure

of H<sub>2</sub>O in the reacting zone is in the range 2.15 to 17.5 Torr corresponding to temperatures - 10 to 20°C using Kr as an internal standard. H<sub>2</sub>O vapor was mixed with variable amounts of He. The iodide ion concentration was in the range 0.5 to 3.0 M.

- (c) Uptake on a train of aqueous NaI droplets (80 to 150 μm) in a laminar flow tube operated in the range 275-293K. The O<sub>3</sub> concentration in the flow tube was measured at m/e 46 (NO<sub>2</sub><sup>+</sup>) after titration by NO and conversion to NO<sub>2</sub>. No measurable uptake of O<sub>3</sub> on pure water was observed. The uptake into aqueous NaI was limited by reaction of O<sub>3</sub> with I<sup>-</sup> as shown by the dependence of γ<sub>ss</sub> on the ionic strength of the solution. From the intercept and linearity of the plot of 1/γ vs. 1/(a<sub>I</sub>)<sup>1/2</sup> Magi et al. (1997) derive a lower limit of α<sub>b</sub> of 0.1.
- (d) The NaCl aerosol had a bimodal distribution (large average diameter: 2-4 μm, small average diameter: <1μm) with typical surface areas and particle number densities in the range of 1 – 6 x 10<sup>-3</sup> cm<sup>2</sup>/cm<sup>3</sup> and 1 -4 x 10<sup>4</sup> particles/cm<sup>3</sup>, respectively. The value of γ is an upper limit and is given for unbuffered and NaCl aerosol buffered at pH=7.2 using NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub>. A slow wall-catalyzed reaction occurred when working with HCl-acidified NaCl aerosol at pH=0.3 resulting in Cl<sub>2</sub>. This reaction presumably occurs on NaCl aerosol particles adhering to the walls of the flow tube.
- (e) Uptake onto a static single drop (2-3 mm in diameter) containing NaI (2 x 10<sup>-2</sup> to 4 M) was monitored by time-resolved UV/Vis absorption spectroscopy in the range 240 to 800 nm. The time-dependent values of the optical density of I<sub>3</sub><sup>-</sup> were analyzed to derive uptake coefficients γ in the range 2.0 x 10<sup>-5</sup> to 1.5 x 10<sup>-2</sup>.
- (f) Aerosol flow tube experiment at atmospheric pressure using deliquesced KI and KI/NaCl aerosol. Aerosol mode ranged from 70 to 573 nm and O<sub>3</sub> concentration detected by CLD) from 70 to 300 ppb. Iodide excess for pseudo first-order conditions could not be maintained in all experiments such that numerical data analysis had to be applied in order to retrieve the bulk accommodation coefficient α<sub>b</sub> and the second-order rate constant k<sup>II</sup> for the liquid phase reaction O<sub>3</sub> + I<sup>-</sup>. The remainder of the parameters for data retrieval is effectively identical to the work of Magi et al. (1997).
- (g) CWFT study at 90 Torr of air coupled to I-CIMS detection of O<sub>3</sub>, H<sub>2</sub>O and Br<sup>2</sup>. O<sub>3</sub> was monitored at 254 nm and was in excess relative to bromide. The detection limit for most negative ions was in the range 10<sup>9</sup>-10<sup>10</sup> molecule cm<sup>-3</sup>. The liquid sample was positioned in a container lying on the bottom of the horizontal flow tube and consisted of an aqueous solution of 0.55 M NaCl and 8.5 mM KBr at pH=1.97 exposed to O<sub>3</sub> at 273 K. Uptake coefficients were derived from the rate of appearance of Br<sub>2</sub> as product assuming no other reactive losses other than the reaction 2Br<sup>-</sup> + O<sub>3</sub> + 2H<sup>+</sup> → Br<sub>2</sub> + O<sub>2</sub> + H<sub>2</sub>O.

### Preferred Values

Parameter	Value for Iodide ion as a reactant	T/K
α <sub>b</sub>	> 0.1	298
k <sup>II</sup> /M <sup>-1</sup> s <sup>-1</sup>	(2.4 ± 1.3) x 10 <sup>9</sup> (average [I <sup>-</sup> ])	293
	(3.2 ± 1.5) x 10 <sup>8</sup>	275
D <sub>l</sub> /cm <sup>2</sup> s <sup>-1</sup>	1.85 x 10 <sup>-5</sup>	293
H/M atm <sup>-1</sup>	1.15 × 10 <sup>-2</sup> exp[2560(1/T-1/298)]	273-293

### Reliability

Δ log (α <sub>b</sub> )	undetermined	298
Δ log (k <sup>II</sup> )	± 0.2	298

Parameter	Value for Bromide ion as a reactant	T/K
$K_{LangC} / \text{cm}^3$ molecule <sup>-1</sup>	$10^{-13}$	233-273
$k_b^{\text{II}} / \text{M}^{-1} \text{s}^{-1}$	$6.3 \times 10^8 \exp(-4450/T)$	273-298
$D_l$	$8.9 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$	273
$H/M \text{atm}^{-1}$	$1.15 \times 10^{-2} \exp[2560(1/T-1/298)]$	273

#### Reliability

$\Delta \log(k^{\text{II}})$	$\pm 0.3$	273-298
$\Delta \log K_{LangC}$	$\pm 0.5$	233-273

#### Comments on Preferred Values

##### O<sub>3</sub> + I<sup>-</sup>

The datasets of Hu et al. (1995), Magi et al. (1997), Rouvière et al. (2010) concur in that the reaction proceeds without a significant surface component and can be described by the following resistor expression:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{\bar{c}}{4HRT\sqrt{k^{\text{II}}a_lD_l}}$$

These studies indicate that  $\alpha_b > 0.1$ .

There is excellent agreement in the retrieved parameters  $\alpha$  and  $k^{\text{II}}$  of Rouvière et al. (2010) and Magi et al. (1997) despite the different types of experiments. The liquid phase rate constant  $k^{\text{II}}$  obtained in both studies agreed with literature values (Garland *et al.* (1980) derive  $2 \times 10^9 \text{M}^{-1} \text{s}^{-1}$  at 298 K) and the values reported by Magi et al. (1997) are recommended. The value of  $k^{\text{II}} = 4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$  at 277 K derived by Hu et al. (1995) seems to be larger by at least a factor of two when compared to literature values for O<sub>3</sub> + I<sup>-</sup>.

The effects of salting out (decrease of H<sub>2</sub>O<sub>3</sub> with increasing scavenger concentration) on  $k^{\text{II}}$  is within the experimental uncertainty of the data and has been ignored in the data evaluation. The values for  $k^{\text{II}}$  displayed in the Table therefore correspond to an average iodide concentration.

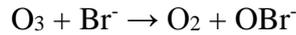
The uptake coefficient of O<sub>3</sub> on deliquescent aerosol containing iodide decreases with increasing coverage of saturated fatty acids depending on the physical and chemical properties of the surfactant (Rouvière and Ammann (2010a)).

##### O<sub>3</sub> + Br<sup>-</sup>

The experiments of Oldridge and Abbatt (2011), the only ones reported in the literature on the interaction of O<sub>3</sub> with liquid aqueous bromide solutions at 273 K, are interpreted in terms of both a surface as well as a bulk reactivity component of excess O<sub>3</sub> reacting with a constant supply of surface bromide in terms of two limiting cases. The surface reaction is invoked, because at low O<sub>3</sub> concentration, the uptake coefficient was about an order of magnitude higher than predicted by bulk reaction alone, and because  $\gamma$  falls off with increasing O<sub>3</sub> concentration similar to other surface reactions analyzed in terms of Langmuir-Hinshelwood kinetics. A concurrent bulk and surface reaction agrees, at least qualitatively, with the laboratory study of Clifford and Donaldson (2007) on the interaction of O<sub>3</sub> with bromide at

the air-aqueous interface in which the authors have studied the occurrence of a pH change at the interface using a surface-adsorbed pH indicator.

The reaction of O<sub>3</sub> with aqueous bromide proceeds via:



We recommend using the bulk reaction rate constant measured by Haag and Hoigné (1983) over the temperature of interest here. At low pH (pH =2 in the experiments by Oldridge and Abbatt), the likely fate of OBr<sup>-</sup> is the reaction of HOBr with bromide or chloride in sea salt to form Br<sub>2</sub> or BrCl, respectively.

The full expression for the uptake coefficient of O<sub>3</sub> to aqueous bromide solutions based on the resistor model including both surface and bulk reaction is:

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s + \left( \frac{1}{\Gamma_{sb}} + \frac{1}{\Gamma_b} \right)^{-1}}$$

Since the bulk accommodation coefficient is likely to be >0.1 and the observed steady state uptake coefficients are 10<sup>-6</sup> at maximum, surface accommodation and surface to bulk transfer are not limiting ( $\alpha_s \gg \gamma$ ;  $\Gamma_{sb} \gg \Gamma_b$ ) and the expression simplifies to:

$$\gamma \approx \Gamma_s + \Gamma_b$$

For the surface reaction, the expression for a Langmuir-Hinshelwood reaction is:

$$\Gamma_s = \frac{4k_s^{II} [\text{Br}^-]_s K_{LangC} N_{max}}{\bar{c} (1 + K_{LangC} [\text{O}_3]_g)}$$

The surface concentration of bromide ions can be estimated by normalizing the bulk mole fraction to the surface density of H<sub>2</sub>O molecules (10<sup>15</sup> molecules cm<sup>-2</sup>), leading to [Br<sup>-</sup>]<sub>s</sub> ≈ 2.9 × 10<sup>12</sup> molecules cm<sup>-2</sup> for the 8.5 mM solution of Oldridge and Abbatt. Since the surface to volume ratio was not varied in these experiments, only the product  $k_s^{II} \times N_{max}$  is constrained by the data for which a value of 0.03 s<sup>-1</sup> is obtained for the best fit. Assuming that  $N_{max}$  is about 10<sup>15</sup> molecules cm<sup>-2</sup>,  $k_s^{II}$  would be a few 10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup>. In turn, the value for  $K_{LangC}$  is well constrained by the inverse O<sub>3</sub> concentration dependence, and the value found by Oldridge and Abbatt is adopted.

The contribution due to uptake due to the bulk reaction can be calculated by:

$$\Gamma_b = \frac{4HRT}{\bar{c}} \sqrt{D_1 k_b^{II} [\text{Br}^-]}$$

In the absence of independent measurements of the solubility of O<sub>3</sub> in halide solutions, we recommend using the expression as compiled by Chameides (1984). The diffusion coefficient given in the Table for 273 K has been extrapolated from its room temperature value via the Stokes-Einstein relation. The parameterization reproduces the experimental data by Oldridge and Abbatt fairly well, even though it overestimates  $\gamma$  at high concentration, because the surface reaction doesn't fall off as quickly. Note that the reacto-diffusive length for deliquesced sea-salt is at least a few tens of  $\mu\text{m}$ , requiring the usage of the correction term for spherical particles. For the atmospherically relevant concentration range (< 10<sup>12</sup> molecules cm<sup>-3</sup>), the shape independent surface reaction term would dominate, though.

Br<sub>2</sub> has been observed as gas-phase product resulting from the interaction of O<sub>3</sub> with frozen and aqueous bromide surfaces (Oum et al., 1998; Hunt et al., 2004).

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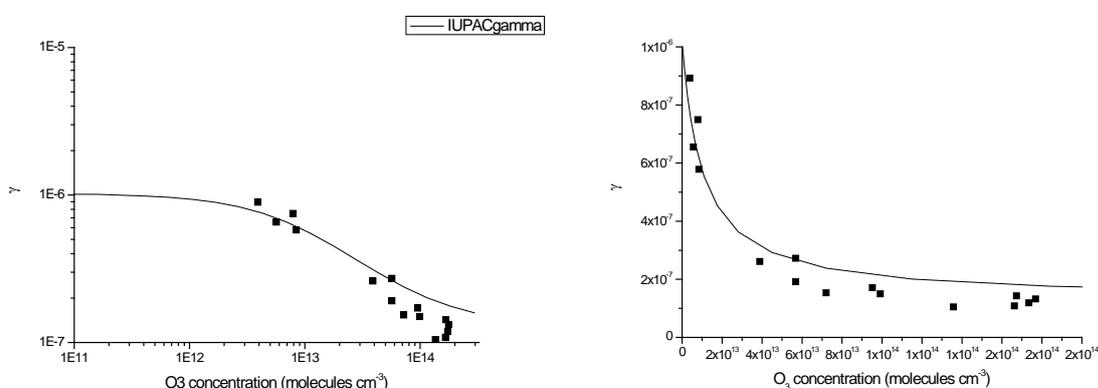


Figure 1: Uptake coefficient of O<sub>3</sub> on 8.5 mM bromide solution (log scale left, linear scale right) derived from Br<sub>2</sub> generated; symbols: data by Oldridge and Abbatt (2011), line: IUPAC recommendation.