

**IUPAC Subcommittee on Gas Kinetic Data Evaluation –
Data Sheet VI.A2.0 HET_SALTS_0**

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O₃ + Cl⁻/Br⁻/I⁻ (aq) → products

Experimental data

<i>Parameter</i>	<i>Temp./K</i>	<i>Reference</i>	<i>Technique/ Comments</i>
<i>Uptake, Accommodation coefficients: γ, α</i>			
$\gamma_{ss} > 2 \times 10^{-3}$ ($\pm 20\%$) (SnCl ₂ 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 ⁻] 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 ⁻)			
$\gamma_0 = 4.4 \times 10^{-4}$ (mixed KI/NaCl aerosol with [I ⁻] = 0.9M, [Cl ⁻] = 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 O₃ (10¹¹ molecule cm⁻³) to a liquid film (20 μm thick). The total pressure was between 13.6 to 14.6 mbar with half of it being H₂O vapor. No uptake of O₃ was observed into pure deionized water, but γ increased as a function of the concentration of the trapping agent (*e.g.*, SnCl₂) to values in the 10⁻² range. The measured loss rate was limited by the diffusion of O₃ to the wetted wall when γ was larger than 0.02 in the presence of solutions of scavengers Na₂SO₃, Na₂S₂O₃ and SnCl₂.
- (b) Droplet diameters in the range 120-250 μm. The concentration of O₃ varied from 5 × 10¹² to 1 × 10¹⁴ molecule cm⁻³ 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 H₂O 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. H₂O 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 O₃ concentration in the flow tube was measured at m/e 46 (NO₂⁺) after titration by NO and conversion to NO₂. No measurable uptake of O₃ on pure water was observed. The uptake into aqueous NaI was limited by reaction of O₃ with I⁻ as shown by the dependence of γ_{ss} on the ionic strength of the solution. From the intercept and linearity of the plot of 1/γ vs. 1/(a_I)^{1/2} Magi et al. (1997) derive a lower limit of α_b 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 10⁻³ cm²/cm³ and 1 -4 x 10⁴ particles/cm³, respectively. The value of γ is an upper limit and is given for unbuffered and NaCl aerosol buffered at pH=7.2 using NaH₂PO₄/Na₂HPO₄. A slow wall-catalyzed reaction occurred when working with HCl-acidified NaCl aerosol at pH=0.3 resulting in Cl₂. 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 10⁻² 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 I₃⁻ were analyzed to derive uptake coefficients γ in the range 2.0 x 10⁻⁵ to 1.5 x 10⁻².
- (f) Aerosol flow tube experiment at atmospheric pressure using deliquesced KI and KI/NaCl aerosol. Aerosol mode ranged from 70 to 573 nm and O₃ 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_b and the second-order rate constant k^{II} for the liquid phase reaction O₃ + I⁻. 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 O₃, H₂O and Br². O₃ was monitored at 254 nm and was in excess relative to bromide. The detection limit for most negative ions was in the range 10⁹-10¹⁰ molecule cm⁻³. 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 O₃ at 273 K. Uptake coefficients were derived from the rate of appearance of Br₂ as product assuming no other reactive losses other than the reaction 2Br⁻ + O₃ + 2H⁺ → Br₂ + O₂ + H₂O.

Preferred Values

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

Reliability

Δ log (α _b)	undetermined	298
Δ log (k ^{II})	± 0.2	298

Parameter	Value for Bromide ion as a reactant	T/K
K_{LangC} / cm^3 molecule ⁻¹	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

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

Comments on Preferred Values

O₃ + I⁻

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 α and k^{II} of Rouvière et al. (2010) and Magi et al. (1997) despite the different types of experiments. The liquid phase rate constant k^{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 O₃ + I⁻.

The effects of salting out (decrease of HO₃ with increasing scavenger concentration) on k^{II} is within the experimental uncertainty of the data and has been ignored in the data evaluation. The values for k^{II} displayed in the Table therefore correspond to an average iodide concentration.

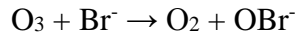
The uptake coefficient of O₃ on deliquescent aerosol containing iodide decreases with increasing coverage of saturated fatty acids depending on the physical and chemical properties of the surfactant (Rouvière and Ammann (2010a)).

O₃ + Br⁻

The experiments of Oldridge and Abbatt (2011), the only ones reported in the literature on the interaction of O₃ 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 O₃ reacting with a constant supply of surface bromide in terms of two limiting cases. The surface reaction is invoked, because at low O₃ concentration, the uptake coefficient was about an order of magnitude higher than predicted by bulk reaction alone, and because γ falls off with increasing O₃ 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 O₃ 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 O₃ 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⁻ is the reaction of HOBr with bromide or chloride in sea salt to form Br₂ or BrCl, respectively.

The full expression for the uptake coefficient of O₃ 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 10⁻⁶ 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 H₂O molecules (10¹⁵ molecules cm⁻²), leading to [Br⁻]_s ≈ 2.9 × 10¹² molecules cm⁻² 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⁻¹ is obtained for the best fit. Assuming that N_{max} is about 10¹⁵ molecules cm⁻², k_s^{II} would be a few 10⁻¹⁷ cm² molecule⁻¹. In turn, the value for K_{LangC} is well constrained by the inverse O₃ 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 O₃ 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 γ 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 μm , requiring the usage of the correction term for spherical particles. For the atmospherically relevant concentration range (< 10¹² molecules cm⁻³), the shape independent surface reaction term would dominate, though.

Br₂ has been observed as gas-phase product resulting from the interaction of O₃ with frozen and aqueous bromide surfaces (Oum et al., 1998; Hunt et al., 2004).

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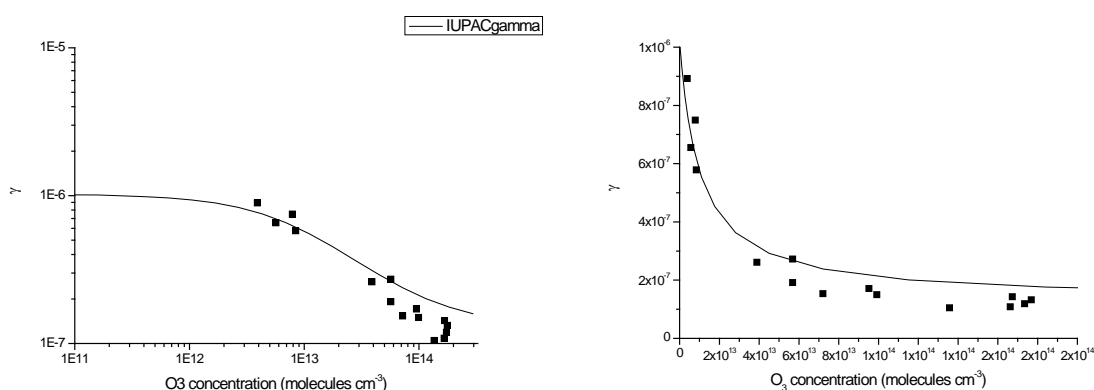


Figure 1: Uptake coefficient of O₃ on 8.5 mM bromide solution (log scale left, linear scale right) derived from Br₂ generated; symbols: data by Oldridge and Abbatt (2011), line: IUPAC recommendation.