

The mass accommodation coefficient of ozone on an aqueous surface

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A wetted-wall cylindrical flow reactor was used to measure uptake coefficients, γ , of O_3 on aqueous surfaces at 293 K. The loss of O_3 from the gas-phase following contact with varying areas of aqueous surface was determined by UV absorption. The use of $Na_2S_2O_3$ as an aqueous-phase scavenger for O_3 ensured that uptake coefficients were in a reaction-controlled rather than mass accommodation-controlled regime. Observed uptake coefficients were corrected for radial gas-diffusion to yield values of γ^{corr} . From extrapolation of a plot of $1/\gamma^{corr}$ against the inverse square-root of the $Na_2S_2O_3$ activity, a value of $\alpha = 4 \times 10^{-2}$ was derived for the true mass accommodation coefficient of O_3 . Evaluation of uncertainties indicate a conservative lower limit of 10^{-2} for α . The data do not rule out that the upper limit approaches unity. However, it is shown that the measured value of α is sufficiently high that mass accommodation does not limit heterogeneous processing of O_3 in the atmosphere for droplets of diameter $>10 \mu m$. A value of $3.7_{-0.6}^{+0.7} \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ is derived for the aqueous-phase reaction rate coefficient between O_3 and $Na_2S_2O_3$ at 293 K.

Introduction

Recent modelling studies have demonstrated the importance of the condensed aqueous phase (rain, cloud, aerosols, dew drops, etc.) to the chemistry and radical budget of the troposphere.¹⁻⁴ A key parameter in quantifying the transport of a species across the interface from the gas phase is the mass accommodation coefficient, α , defined as the probability that an individual molecule striking the liquid surface enters the bulk liquid. Estimates of α are frequently used in models due to the lack of experimental data.^{4,5} Ozone is a key species in the troposphere, acting as an important oxidant in both the gas and aqueous phases. The source of O_3 in the aqueous phase is uptake from the gas phase. Although there have been previous experimental measurements of α for O_3 , there remains considerable variation in the values published in the literature, which was the motivation for the α measurement reported here.

Mass accommodation coefficients are usually derived from experiments which determine the fraction of molecules removed from the gas phase under particular well-controlled conditions. This yields an overall uptake coefficient, γ , that represents the observed net transport across the interface, incorporating flux due to gas phase diffusion to the surface, the mass accommodation coefficient, diffusion in the liquid phase, and reaction in the liquid phase, if appropriate. The uptake coefficient is usefully approximated by the resistance model formulation,⁶

$$\frac{1}{\gamma} = \frac{1}{\Gamma_G} + \frac{1}{\alpha} + \frac{1}{\Gamma_{SOL} + \Gamma_{RXN}} \quad (1)$$

in which, by analogy to the terminology of an electric circuit, $1/\alpha$ is the resistance to mass transfer due to interfacial transfer, and $1/\Gamma_G$, $1/\Gamma_{SOL}$ and $1/\Gamma_{RXN}$ are the resistances to mass transfer due to gas phase diffusion to the surface, liquid solubility and liquid phase reaction, respectively. The quantities Γ_G , Γ_{SOL} and Γ_{RXN} are the corresponding conductances, or dimensionless mass transfer coefficients. Expressions for the

liquid solubility and reaction mass transfer coefficients have been derived:⁶

$$\Gamma_{SOL} = \frac{4HRT}{\pi^{1/2}\omega} \sqrt{\frac{D_L}{t}} \quad (2)$$

$$\Gamma_{RXN} = \frac{4HRT\sqrt{D_L}k_{RXN}}{\omega} \quad (3)$$

where T is the temperature, H is the Henry's law coefficient of the trace species, D_L is its diffusion coefficient in the liquid, R is the universal gas constant, t is the liquid-gas contact time, $\omega = \sqrt{8RT/\pi M}$ (where M is the molar mass) is the mean molecular velocity of the trace species in the gas phase, and k_{RXN} is the pseudo-first order rate coefficient for a reaction between the transferred species and a reactant in the liquid. The expression for the gas diffusion transfer coefficient, Γ_G , depends on the specific geometry of the contact surface between gas and liquid phases. In this work, a cylindrical wetted-wall flow reactor was used to measure uptake coefficients for O_3 at 293 K. Using the well-established diffusion theory for gas diffusion in cylindrical geometry it is possible to correct experimental uptake coefficients for any limitation to net surface uptake imposed by insufficient rate of radial gas diffusion (see Results section for details). The resulting γ^{corr} values correspond to removal of the $1/\Gamma_G$ term from the expression for $1/\gamma$ in eqn. (1).

Ozone neither reacts with pure water nor is particularly soluble in water. The Henry's law coefficient at 293 K is $1.3 \times 10^{-2} \text{ M atm}^{-1}$.⁷ Therefore uptake of O_3 onto pure water surfaces rapidly leads to liquid saturation. However, by adding a suitable scavenger reagent to the aqueous phase to react with O_3 it is possible to ensure that $\Gamma_{RXN} \gg \Gamma_{SOL}$, i.e. that Henry's law solubility is not reached on the timescale of liquid-gas exposure. Eqn. (1) then simplifies to,

$$\frac{1}{\gamma^{corr}} = \frac{1}{\alpha} + \frac{\omega}{4HRT\sqrt{D_L}k_{RXN}} \quad (4)$$

and the observed (gas diffusion corrected) uptake is a function only of the rate of reaction with the scavenger and not of the contact time between gas and liquid. In this work, $\text{Na}_2\text{S}_2\text{O}_3$ was added to the water as a reactive scavenger for O_3 .

Experimental

The wetted-wall reactor consisted of a vertically mounted tube, through which O_3 entrained in He flowed, whose internal walls were covered by a thin aqueous film continuously flowing down under the influence of gravity. The experimental set has been described previously by Müller and Heal.⁸

The glass reactor was about 90 cm long, with 1.6 cm internal diameter, and surrounded by a jacket through which coolant could flow. The aqueous solution for the exposed surface was pumped to the reactor by a digital liquid pump (L/S Masterflex with pulse dampener) and filled an annular reservoir at the top of the flow tube. The solution spilled evenly over the lip of the reservoir to form a thin film of flowing liquid, uniformly wetting the entire inner surface of the flow tube. The solution was collected at the bottom of the reactor into a 6 L flask, which was cooled by an ice-salt mixture to a temperature of about -15°C to prevent back streaming of water vapour into the flow tube. The assumption of uniform wetting of the whole inside wall of the reactor is essential for the data analysis. Experiments were performed only when visual inspection confirmed the wall was completely wetted. Also, since rippling enhances surface absorption rates,⁹ experiments were always conducted in a non-rippling regime (solution flow rates $<150\text{ mL min}^{-1}$).

The main flow of He carrier gas entered the reactor through a side-arm at the top. The gas was humidified before entering the reactor to avoid evaporative cooling of the water film and to maintain a well-defined temperature in the reactor. O_3 entered along the centre-line of the reactor through a movable glass injector with an inner diameter of 3 mm. Different exposure times between O_3 and liquid surface were achieved by varying the injector position. The O_3 -He mix exited the reactor through a side arm below the wetted film and into a UV absorption cell. All gas flow rates were controlled by calibrated mass flow controllers (Tylan, FC 280 SA). The relative humidity in the reactor was measured using a humidity meter (Vaisala, HMP 234). The temperature of the flowing liquid and the gas were confirmed with thermocouples at the bottom of the reactor. The gas temperature was cross-checked by comparing it with the temperature reading at the humidity meter.

The flow reactor was operated at low pressures, typically a few tens of torr, in order to minimise the magnitude of corrections to observed uptakes arising from radial gas diffusion limitations. Gas pressure was monitored using capacitance manometers (Edwards, Barocel 600AB) at the top of the flow tube and at the UV absorption cell. Linear gas velocities in the reactor (required to convert injector position to gas-surface contact time) were calculated for each experiment taking into account the contribution of water vapour to total gas flow. A typical gas velocity of $\sim 500\text{ cm s}^{-1}$ corresponded to a contact time of $\sim 20\text{ ms}$ per 10 cm length exposure to the wetted film. The upper 15–20 cm of aqueous film was not used for uptake measurements in order to allow thorough mixing and equilibration of water vapour and He.

Changes in O_3 gas concentrations following exposure to the aqueous surface were measured by UV absorption at 253.7 nm. Light from a 150 W Xe lamp (Osram, XBO) was dispersed, after passing through the 90 cm length absorption cell, by a 300 groove mm^{-1} grating (in an Instruments SA 270M Imaging Spectrograph) onto a 1024 element photodiode array (Instrument SA, QuikScan). The integrated software package (Instrument SA, SpectraMax) was used for the control of the spectrograph and for data acquisition. Fig. 1 shows an exam-

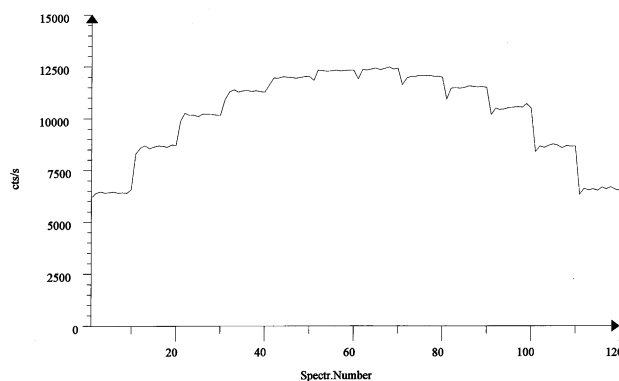


Fig. 1 Example change in absorption signal with change in injector position. 10 spectra were recorded at each of 6 injector positions. The injector was moved out (increasing gas-liquid contact time) for spectra 1 to 60 and moved in for spectra 61 to 120.

ple of the change in light intensity incident on the photodiode array as the injector is moved in and out of the reactor.

Ozone was produced from a flow of oxygen through an electric-discharge generator (Argentox, GL 10) and absorbed on silica gel in a dry ice-ethanol trap ($\sim 195\text{ K}$). Mixtures of O_3 in He were prepared on a vacuum line. Solutions of $\text{Na}_2\text{S}_2\text{O}_3$, (Acros, $>99\%$) used as the scavenger for O_3 varied in concentration between 0.02 and 0.20 M.

Results

The loss of O_3 from the gas phase by uptake at the internal surface of a cylindrical flow reactor is a first-order process,

$$\frac{d[\text{O}_3]}{dt'} = -k_w[\text{O}_3] \quad (5)$$

where k_w is the first-order rate coefficient and t' is the exposure time between gas and liquid surface, which was proportional to injector position up the flow reactor. Since gas phase $[\text{O}_3]$ was directly proportional to absorbance in the absorption cell, values of k_w were determined from the gradients of plots of $\ln(\text{absorbance})$ versus injector position, as shown in Fig. 2. However, if experimental conditions were such that surface uptake was large and/or radial gas diffusion was small, observed k_w underestimated the true first-order rate coefficient because radial diffusion was insufficient to maintain the neces-

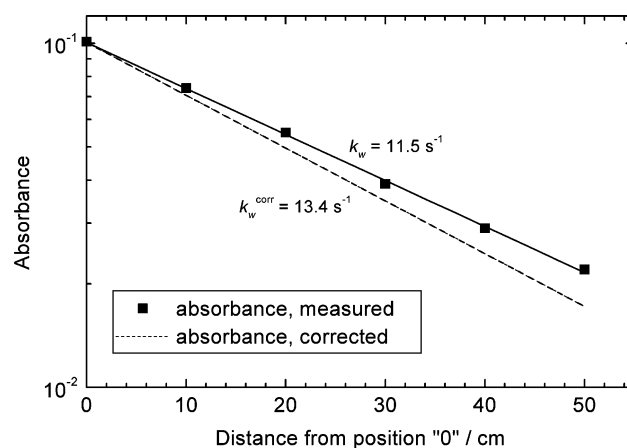


Fig. 2 Log-linear plot of absorbance against injector position before (solid line) and after (dashed line) correction for radial gas-phase O_3 concentration gradient, as outlined in the text. Injector position is converted to contact time of gas with liquid surface via the gas velocity (in this experiment, 379 cm s^{-1}).

Table 1 Experimental parameters and results for uptake measurements of O₃ onto Na₂S₂O₃ solutions at 293 K

Total pressure p/Torr	Concentration [Na ₂ S ₂ O ₃]/mol l ⁻¹	Activity coefficient $\gamma_{\text{Na}_2\text{S}_2\text{O}_3}$	$(c^\ominus a_{\text{Na}_2\text{S}_2\text{O}_3})/\text{mol l}^{-1}$	k_w/s^{-1}	$k_w^{\text{corr}}/\text{s}^{-1}$	Corrected uptake coefficient γ^{corr}
12.0	0.1990	0.393	0.07820	17.6	21.8	9.73×10^{-4}
17.1	0.0991	0.464	0.04595	12.8	15.3	6.84×10^{-4}
19.0	0.0763	0.485	0.03699	10.2	11.8	5.54×10^{-4}
15.0	0.0598	0.504	0.03016	11.5	13.4	5.98×10^{-4}
17.1	0.0410	0.539	0.02209	8.9	10.0	4.48×10^{-4}
19.6	0.0359	0.553	0.01984	8.8	10.0	4.48×10^{-4}
18.0	0.0309	0.571	0.01763	8.5	9.5	4.25×10^{-4}
18.0	0.0309	0.571	0.01763	8.4	9.5	4.22×10^{-4}
14.0	0.0203	0.627	0.01270	7.5	8.2	3.75×10^{-4}

sary flux of O₃ molecules to the surface. This corresponds to a significant gas-phase diffusion resistance term, $1/\Gamma_G$, in eqn. (1). The observed values of k_w were therefore corrected for the effect of a radial concentration gradient to yield k_w^{corr} , using a computer program following the algorithm of Brown.¹⁰ An example correction is shown in Fig. 2. Finally, the gas-corrected uptake coefficient, γ^{corr} , corresponding to the first-order loss coefficient in cylindrical geometry was calculated from,

$$\gamma^{\text{corr}} = \frac{2rk_w^{\text{corr}}}{\omega} \quad (6)$$

where r was the radius of the reactor.¹¹ The pressure-independent binary gas diffusion coefficients of O₃ in water vapour and He required for the correction method of Brown were calculated to be 175 Torr cm² s⁻¹ and 507 Torr cm² s⁻¹, respectively, using the Fuller–Schettler–Giddings estimation method.¹²

Assuming that the reaction between O₃ and Na₂S₂O₃ is second-order with rate coefficient, k'' , and that Na₂S₂O₃ is in excess, yields, from eqn. (4),

$$\frac{1}{\gamma^{\text{corr}}} = \frac{1}{\alpha} + \frac{\omega}{4HRT\sqrt{D_L k'' c^\ominus a_{\text{Na}_2\text{S}_2\text{O}_3}}} \quad (7)$$

where $a_{\text{Na}_2\text{S}_2\text{O}_3}$ is the dimensionless activity of Na₂S₂O₃ and c^\ominus is the standard concentration of 1.0 mol L⁻¹. The activity and concentration of Na₂S₂O₃ are related through,

$$a_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{\gamma_{\text{Na}_2\text{S}_2\text{O}_3} [\text{Na}_2\text{S}_2\text{O}_3]}{c^\ominus} \quad (8)$$

where $\gamma_{\text{Na}_2\text{S}_2\text{O}_3}$ is the activity coefficient. Values of $\gamma_{\text{Na}_2\text{S}_2\text{O}_3}$ were obtained from Robinson and Stokes.¹³ Measurements of uptake were repeated for different concentrations of Na₂S₂O₃ and the relevant experimental data and results are given in Table 1.

Eqn. (7) indicates that a plot of $\log(\gamma^{\text{corr}})$ against $\log(c^\ominus a_{\text{Na}_2\text{S}_2\text{O}_3})$ should be a straight line with gradient 0.5 if uptake experiments were conducted in a reaction-controlled rather than mass accommodation-controlled regime, *i.e.* for $\omega/(4HRT\sqrt{D_L k'' c^\ominus a_{\text{Na}_2\text{S}_2\text{O}_3}}) \gg 1/\alpha$. Fig. 3 shows this plot for the experiments presented here. The linearity of the data (correlation coefficient, $r = 0.98$) and the gradient of 0.52 ± 0.05 confirm that the measured uptake coefficient of O₃ was not limited by mass accommodation, *i.e.* that α must significantly exceed the observed uptake coefficient even for the highest concentrations of Na₂S₂O₃ scavenger used. From Table 1 it is therefore possible to conclude that α must certainly exceed 10^{-3} .

Eqn. (7) also indicates that a plot of $1/\gamma^{\text{corr}}$ against $1/\sqrt{c^\ominus a_{\text{Na}_2\text{S}_2\text{O}_3}}$ should be a straight line of gradient $\omega/(4HRT\sqrt{D_L k''})$ and intercept $1/\alpha$, and this is shown in Fig. 4. The intercept of 24 yields a value of $\alpha = 4 \times 10^{-2}$. The statistical error in the intercept from the regression yields a lower limit of $\alpha \sim 3 \times 10^{-3}$ (at 95% confidence). However, for

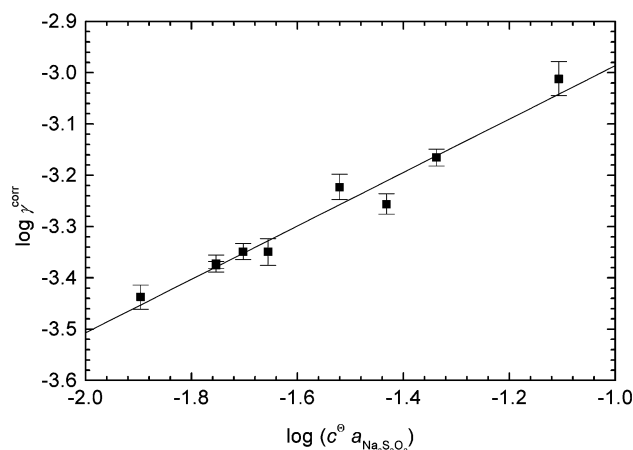


Fig. 3 Plot of $\log(\gamma^{\text{corr}})$ against $\log(c^\ominus a_{\text{Na}_2\text{S}_2\text{O}_3})$ for the gas-diffusion corrected reactive uptake of O₃ on Na₂S₂O₃ solution at 293 K. The error bars of the individual points are the statistical errors only in the fits of the plots to derived values of k_w . The solid line is the least-squares linear fit to the data ($r = 0.98$) and has a gradient of 0.52 ± 0.05 (standard error of slope).

resistance due to mass accommodation to be small in comparison with resistance due to liquid reaction (values of ≥ 1000 for the latter are obtained by substituting data appropriate to the experimental conditions into the expression for $1/\Gamma_{\text{RXN}}$),

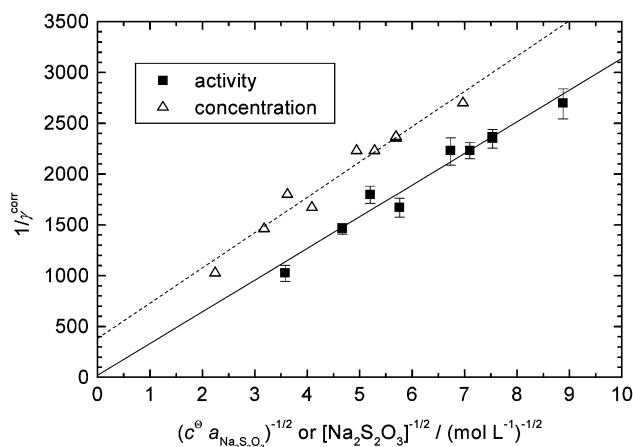


Fig. 4 Plot of $1/\gamma^{\text{corr}}$ against $1/\sqrt{c^\ominus a_{\text{Na}_2\text{S}_2\text{O}_3}}$ (squares) and against $1/\sqrt{[\text{Na}_2\text{S}_2\text{O}_3]}$ (triangles). The solid and dashed lines are linear fits to the activity and concentration data, respectively. The slope and intercept of the former have values $310 \text{ mol}^{1/2} \text{ L}^{-1/2}$ and 24, and correspond to $\omega/(4HRT\sqrt{D_L k''})$ and $1/\alpha$, respectively. The error bars of the individual points are the statistical errors only in the fits of the plots to derived values of k_w .

requires a more appropriate lower limit to α of $\sim 10^{-2}$. The upper uncertainty limit to α derived from Fig. 4 corresponds to a negative intercept, which is not physically possible. The statistical uncertainties are large because the extrapolation of the data to the intercept is extremely sensitive to the linear fit. Overall, however, the best estimate from these data is that $\alpha \sim 4 \times 10^{-2}$ but that the error range encompasses values from 10^{-2} towards unity.

The gradient of $310 \text{ mol}^{1/2} \text{ L}^{-1/2}$ in Fig. 4 yields a value of $k'' = (3.7_{-0.6}^{+0.7}) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ for the aqueous-phase reaction between O_3 and $\text{Na}_2\text{S}_2\text{O}_3$ at 293 K. The method of Wilke and Chang, as described in Reid *et al.*,¹² was used to calculate the liquid diffusion coefficient of $D_L = 2.30 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for O_3 in water at 293 K required to derive k'' . A Henry's law coefficient of $H = 1.3 \times 10^{-2} \text{ M atm}^{-1}$ at 293 K was derived from Kosak-Channing and Helz.⁷ The quoted uncertainties are the statistical errors in the linear regression in Fig. 4.

Discussion

Possible sources of measurement error in γ and α

The major potential source of error is variation in the relative humidity of the gas flow which is required to calculate the gas velocity and the overall gas diffusion coefficient. These parameters impact on the derivation of k_w and k_w^{corr} , and ultimately of γ^{corr} and α . Relative humidity is a strong function of temperature, hence the need for accurate and precise control of the experimental conditions in the flow tube. A realistic estimate of the overall error in γ^{corr} due to uncertainties in the relative humidity and minor fluctuations in temperature and pressure along the flow tube is $\pm 20\%$. Propagating these uncertainties does not affect the overall estimate for $\alpha > 10^{-2}$ discussed above.

Salt activity

Some researchers neglect to use activity in the data treatment for reactive uptake and use concentrations instead. For example, Fickert *et al.*¹⁴ used $[\text{Br}^-]$ up to 0.1 M when investigating uptake of ClNO_2 . The effect on the data analysis of using concentrations rather than activities for the work presented here is shown as the dashed line in Fig. 4. The intercept of this plot yields $\alpha = 2.6 \times 10^{-3}$. The difference in α between the two approaches is significant (about a factor of 16). The implied resistance of 385 due to mass accommodation ($1/\alpha$) obtained from the concentration plot is not credible given that it has already been shown that uptake in these experiments was in the reaction-controlled regime. This shows it is important that activities rather than concentrations are used in all analyses.

The possible effect of ionic strength on the liquid diffusion coefficient must also be considered. Akita¹⁵ has presented a method to predict diffusivities of gases in aqueous electrolyte solutions, if gas diffusivities in pure water and the densities of the solutions are available. Application of the method to the experimental conditions here decreased the liquid diffusion coefficient of O_3 in $\text{Na}_2\text{S}_2\text{O}_3$ by about 5% to $D_L = 2.18 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Although the modification is systematic, it is within the general uncertainty range of the Wilke and Chang estimation method¹² and can therefore be ignored.

Effect of ionic strength on Henry's law coefficient

The effect on the Henry's law coefficient for O_3 from the presence of $\text{Na}_2\text{S}_2\text{O}_3$ in the solution should also be considered. The scavenger concentrations used in this study ranged from 0.02 to 0.2 mol L^{-1} which correspond to ionic strengths of 0.06 to 0.6 mol L^{-1} . Although data are not available specifically for $\text{Na}_2\text{S}_2\text{O}_3$, Kosak-Channing and Helz⁷ reported the

Table 2 Estimated Henry's law coefficient of O_3 in $\text{Na}_2\text{S}_2\text{O}_3$ at 293 K as a function of ionic strength. k_S'' is the rate coefficient of ozone with $\text{Na}_2\text{S}_2\text{O}_3$ in electrolyte

$[\text{Na}_2\text{S}_2\text{O}_3]/\text{mol L}^{-1}$	$I_S/\text{mol L}^{-1}$	$H_S^{\text{O}_3}/\text{M atm}^{-1}$	$k_S''/\text{L mol}^{-1} \text{ s}^{-1}$
0.1990	0.597	1.081×10^{-2}	5.3×10^8
0.0991	0.297	1.186×10^{-2}	4.4×10^8
0.0763	0.229	1.211×10^{-2}	4.2×10^8
0.0598	0.180	1.230×10^{-2}	4.1×10^8
0.0410	0.123	1.252×10^{-2}	4.0×10^8
0.0359	0.108	1.258×10^{-2}	3.9×10^8
0.0309	0.093	1.263×10^{-2}	3.9×10^8
0.0203	0.061	1.276×10^{-2}	3.8×10^8

change in Henry's law coefficient of O_3 with ionic strength using solutions of Na_2SO_4 .

The Henry's law coefficient of ozone in ionic solution, $H_S^{\text{O}_3}$, for the salt concentrations used here were calculated from the Setchenow expression, using data for Na_2SO_4 as a surrogate for $\text{Na}_2\text{S}_2\text{O}_3$, *i.e.*

$$\log \frac{H^{\text{O}_3}}{H_S^{\text{O}_3}} = k_S [\text{Na}_2\text{SO}_4] \quad (9)$$

where H^{O_3} and $H_S^{\text{O}_3}$ are the Henry's law coefficient of ozone in pure water and in the salt solution, respectively, $[\text{Na}_2\text{SO}_4]$ is the molarity of the Na_2SO_4 solution and k_S is the Setchenow salting-out coefficient (L mol^{-1}). The quantity k_S can be described as the sum of contributions of the negative and positive species in solution and of the gas⁹

$$k_S = k_S^{\text{Na}^+} + k_S^{\text{SO}_4^{2-}} + k_S^{\text{O}_3} \quad (10)$$

Values for $k_S^{\text{Na}^+}$ and $k_S^{\text{SO}_4^{2-}}$ were taken from Danckwerts⁹ and are independent of temperature. Magi *et al.*¹⁶ provide a value of $k_S^{\text{O}_3}$ at 293 K, based on the results of Kosak-Channing and Helz⁷ for Na_2SO_4 solutions. This leads to a value of $k_S = 0.134 \text{ L mol}^{-1}$. Values of $H_S^{\text{O}_3}$ calculated for the different experimental salt concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ used in this study are given in Table 2. Both approaches to calculating $H_S^{\text{O}_3}$, namely, calculation *via* salting-out coefficients of single ions and the experimental values determined for four ionic strength by Kosak-Channing and Helz⁷ agree.

Since the slope of the solid line in Fig. 4 is linear, the product $H_S^{\text{O}_3} \sqrt{k_S''}$ is constant and the second-order rate constant k_S'' in the electrolyte can be calculated which takes into account the ionic strength. These calculated values for k_S'' are listed in Table 2 and they increase with ionic strength. However, all values of k_S'' are within the error limit of k'' , apart from at the highest ionic strength. Therefore, the effect of ionic strength on Henry's law coefficient was neglected.

Comparison with previous measurements

The combined interpretation of the data from Table 1 and Figs. 3 and 4 place a likely lower limit of 10^{-2} on α for O_3 on water at 293 K. A better estimate is 4×10^{-2} , but the value may be closer to unity.

Published values of α and k'' are compared in Table 3. The value of $\alpha = \sim 4 \times 10^{-2}$ (lower limit $> 10^{-2}$) obtained in this work is consistent with the measurements by Utter *et al.*,¹⁷ Hu *et al.*¹⁸ and Magi *et al.*¹⁶ The latter two studies estimate values of 10^{-1} or greater. It is now clear that the early measurements of α by Tang and Lee¹⁹ and by Wunderlich, as cited in Magi *et al.*,¹⁶ are far too low. In fact, the value from this work agrees very well with the value of $\alpha > 2 \times 10^{-2}$ published by Schütze and Herrmann²⁰ just as this manuscript was being prepared, and both measurements support the value of $\alpha = 5 \times 10^{-2}$ currently specified for O_3 in the detailed

Table 3 Comparison of values of O₃ mass accommodation coefficient and liquid scavenger rate coefficients

α	T/K	Comment	Liquid scavenger species	k'' for reaction of O ₃ with scavenger /L mol ⁻¹ s ⁻¹	Reference
2×10^{-3} to 1	276		SO ₃ ²⁻ S ₂ O ₃ ²⁻ Sn ²⁺	3.9×10^8 2.2×10^8 8.5×10^8	Utter <i>et al.</i> ¹⁷
0.1	277	Considered an estimate	I ⁻	4×10^9	Hu <i>et al.</i> ¹⁸
0.1	281	As lower limit	I ⁻	3.2×10^8 (at 275 K) to 2.4×10^9 (at 293 K)	Magi <i>et al.</i> ¹⁶
5.3×10^{-4}	283		SO ₃ ²⁻		Tang and Lee ¹⁹
5×10^{-3}	RT	Possibly underestimated (low k'')	I ⁻	1×10^6	Wunderlich as cited in Magi <i>et al.</i> ¹⁶
4×10^{-2}	293		S ₂ O ₃ ²⁻	3.7×10^8	This work
$>2 \times 10^{-2}$	298		I ⁻	9.6×10^9 (L ² mol ⁻² s ⁻¹)	Schütze and Herrmann ²⁰

CAPRAM mechanism for tropospheric multiphase chemistry.⁴

The only previous measurement of k'' for the aqueous-phase reaction between O₃ and Na₂S₂O₃ is a value of 2.2×10^8 L mol⁻¹ s⁻¹ at 276 K.¹⁷ Combining this with the value 3.7×10^8 L mol⁻¹ s⁻¹ obtained here at 293 K, and assuming that the temperature dependence of the reaction is described by the Arrhenius equation yields an activation energy for the reaction of ~ 20 kJ mol⁻¹. The calculation is of very limited confidence, of course, since measurements at only two temperatures are available.

Conclusion

Although some uncertainty still remains as to the precise value of α for O₃ it is now clear that it must exceed a few percent. The value of Γ_G for gas-phase diffusion to the surface of a spherical droplet is⁶

$$\Gamma_G = \left(\frac{\omega d}{8D_G} - \frac{1}{2} \right)^{-1} \quad (11)$$

where d is the diameter of the droplet and D_G is the diffusion coefficient of the species in air. Therefore, mass accommodation limits the rate of mass transfer across the interface when $\alpha < \Gamma_G$, or when droplet diameter,

$$d < \frac{8D_G}{\omega} \left(\frac{1}{\alpha} + \frac{1}{2} \right) \quad (12)$$

Substituting $\alpha \sim 0.04$, $\omega \sim 3.6 \times 10^4$ cm s⁻¹ and $D_G \sim 0.2$ cm² s⁻¹ for O₃ in air at 1 atm into eqn. (12) shows that the interfacial transfer of O₃ under atmospheric conditions is limited by mass accommodation only for droplets of diameter < 10 μ m. Since the majority of tropospheric water content resides in droplets of diameters > 10 μ m it can be concluded that the rate of heterogeneous processing of O₃ is controlled by whichever is the slower of gas-phase diffusion to the surface or liquid-phase reaction. However, models that specifically intend to consider O₃ heterogeneous processes on the fraction of the aqueous

aerosol distribution with $d < 10$ μ m must explicitly take mass accommodation into account.

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