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Study of the heterogeneous reaction of O_3 with CH_3SCH_3 using the wetted-wall flowtube technique

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Abstract

This work presents the heterogeneous kinetics of the reaction of CH_3SCH_3 (dimethyl sulphide, DMS) with O_3 (ozone) in aqueous solution at different ionic strengths (0, 0.1 and 1.0 M NaCl) using the wetted-wall flowtube (WWFT) technique. Henry's law coefficients of DMS were determined on pure water and on different concentrations of NaCl (0.1 M–4.0 M) in the WWFT from UV spectrophotometric measurements of DMS in the gas phase using a numerical transport model of phase exchange to be H (M atm^{-1}) = 2.16±0.5 at 274.4 K, 1.47±0.3 at 283.4 K, 0.72±0.2 at 291 K, 0.57±0.1 at 303.4 K and 0.33±0.1 at 313.4 K on water, on 1.0 M NaCl to be H = 1.57±0.4 at 275.7 K, 0.8±0.2 at 291 K and on 4.0 M NaCl to be H = 0.44±0.1 at 275.7 K and 0.16±0.04 at 291 K, showing a significant effect of ionic strength, μ, on the solubility of DMS according to the equation $\ln H = -4061\ T^{-1} + 0.052\ \mu^2 + 50.9\ \mu\ T^{-1} + 14.0$. At concentrations of $DMS_{(liq)}$ above 50 μM, UV spectrophotometry of both $O_{3(gas)}$ and $DMS_{(gas)}$ enables us to observe simultaneously the reactive uptake of O_3 on DMS solution and the gas-liquid equilibration of DMS along the flowtube. The uptake coefficient, γ, of O_3 on aqueous solutions of DMS, varying between 1 and $15 \cdot 10^{-6}$, showed a square root-dependence on the aqueous DMS concentration (as expected for diffusive penetration into the surface film, where the reaction takes place in aqueous solution). It was smaller on NaCl solution in accord with the lower solubility of O_3. The heterogeneous reaction of $O_{3(gas)}$ with $DMS_{(liq)}$ was evaluated from the observations of the second order rate constant (k^{II}) for the homogeneous aqueous reaction $O_{3(liq)} + DMS_{(liq)}$ using a numerical model of radial diffusion and reactive penetration and leading to k^{II} (in units of $10^8\ M^{-1}\ s^{-1}$) = 4.1±1.2 at 291.0 K, 2.15±0.65 at 283.4 K and 1.8±0.5 at 274.4 K. Aside from the expected influence on solubility and aqueous-phase diffusion coefficient of both gases there was no significant effect of ionic strength on k^{II}, that was determined for 0.1 M NaCl, leading to k^{II} ($10^8\ M^{-1}\ s^{-1}$) = 3.2±1.0 at 288 K, 1.7±0.5 at 282 K and 1.3±0.4 at 276 K, and for 1.0 M NaCl, leading to 3.2±1.0 at 288 K, 1.3±0.4 at 282 K and 1.2±0.4 at 276 K, where the error limits include uncertainties of Henry's law constants and dif-

fusion coefficients for DMS and O_3.

1. Introduction

The atmospheric oxidation of dimethyl sulphide (DMS) plays an important role in nature considering the climatic consequences of the cloud-forming products of this oxidation for the global radiation budget with a large contribution of heterogeneous reactions in the lower atmosphere and also in terms of acid deposition, formation of marine aerosol and in the Earth's energy balance (Charlson et al., 1987; Chin et al., 1996; Neubauer et al., 1996; Sciare et al., 2000). The dynamics of the ocean mixed- layer is known to influence sea-to-air exchange of DMS at high latitudes, and seawater concentrations and the vertical distribution of DMS are required to distinguish the impact of the heterogeneous chemistry from meteorological effects (Jodwalis et al., 2000).

In addition, the interaction between sulphur and halogen chemistry has been discussed in recent work, where DMS has been found to react with the BrO radical, indicating that BrO could be another important sink for DMS in the marine atmosphere, forming readily soluble dimethyl sulphoxide (DMSO) by the reaction cycle: $BrO + (CH_3)_2S \rightarrow Br + (CH_3)_2SO$ and $Br + O_3 \rightarrow BrO + O_2$. This cycle corresponds to the net reaction $(CH_3)_2S + O_3 \rightarrow (CH_3)_2SO + O_2$, destroying ozone and recycling BrO to Br (see Toumi, 1994; Bedjanian et al., 1996; Ingham et al., 1999; von Glasow, 2001). The tropospheric reaction DMS + Cl has been also discussed (Chen et al., 2000), however the contribution of this reaction to the atmospheric oxidation of DMS is not clear because the model calculations show a very small difference between the contribution of this reaction in comparison with the reaction BrO + DMS → Br + DMSO (von Glasow et al., 2002). Another link of the chemistry between sulphur and halogen has been also suggested in terms of DMS reaction with HOCl and HOBr in the production of sulphate in the sea-salt aerosol (Vogt et al., 1996).

As pointed out by Gershenzon et al. 2001, comparing the gas-phase reactions OH + DMS ($k \sim 2.6 \cdot 10^9\ M^{-1}\ s^{-1}$, Atkinson et al. 1997) and NO_3 + DMS ($k = 8.5 \cdot 10^8$

M^{-1} s^{-1}, Atkinson et al. 1997) with O_3 + DMS ($k \sim 5.0 \cdot 10^2$ M^{-1} s^{-1}, Atkinson et al. 1997), the latter gas-phase reaction is by far too slow to be atmospherically significant. The same reaction O_3 + DMS is extremely fast in the aqueous phase, 3 to $7 \cdot 10^8$ M^{-1} s^{-1} (Lee and Zhou, 1994; Gershenzon et al. 2001), leading to DMSO as a first stable intermediate. Studies on the oxidation of DMS in the troposphere (Barone et al., 1996) suggested that the combination of the reactions OH + DMS and NO_3 + DMS can be predominating channels for the consumption of DMS in the atmosphere, in agreement with recent work (Falbe-Hansen et al., 2000), that suggests the reactions DMSO + Cl and DMSO + NO_3 to be important as well, but typical mixing ratios and the obtained rate constants indicate that the reaction with OH should be at least two orders of magnitude faster than with NO_3 or Cl. The formation of methanesulphonic acid (MSA) in the coastal Antarctic boundary layer due to the oxidation of DMS by OH has been measured (Jefferson et al., 1998), showing that MSA is formed in an atmospheric buffer layer above the boundary layer, followed by condensation of gas phase MSA on aerosols and transport back to the boundary layer. Heterogeneous aqueous-phase reactions of DMSO, CH_3SO_2H (MSIA) and MSA contribute to the oxidation of DMS and decrease the yield of SO_2, that is the relatively long-lived gaseous precursor of H_2SO_4 in the marine boundary layer and increases the yield of non-sea-salt sulphate, nss – $SO_4^=$ (Campolongo et al., 1999). The kinetics and mechanism of DMSO + OH ($k = 4.5 \cdot 10^9$ $M^{-1}s^{-1}$) in aqueous phase have been recently discussed (Bardouki et al., 2002), indicating that this reaction of DMSO could also influence the particle growth processes. DMSO is therefore an important but indirect source of nss – $SO_4^=$ in the marine atmosphere through heterogeneous processes, as is proposed by different authors (Koga and Tanaka, 1993; Barnes et al., 1994). The present study reinvestigates Henry's law coefficient and the heterogeneous reaction of DMS with ozone by employing the wetted-wall flowtube technique and experimental conditions relevant to marine boundary layer (low temperature and high salinity).

2. Experimental and data evaluation

DMS (99+%) and NaCl (99+%) Aldrich were used as received. NO_{x-} free O_3 was produced by photolysis of O_2 in purified air at 185 nm by a mercury low-pressure lamp (Penray). The solutions were prepared in bidistilled water made of deionized water. The concentrations of O_3 and DMS in aqueous and gas phase were obtained using the reference data (aqueous molar absorptivities and gaseous absorption cross-sections) given in Table 1. The concentration of gaseous O_3 was determined from UV spectra by a Kontron Uvikon 860 spectrophotometer or by a Dasibi O_3-analyzer/generator (model 1009-CP, employing UV absorption at the 254 nm Hg line). A noise limit/analytical error of 2 ppb was estimated for the Dasibi analyser. Both concentrations of DMS, in aqueous and gaseous phase, were obtained by the Uvikon 860 spectrometer at a resolution of 2 nm in quartz cells at $l = 1$ cm (liquid sample of 1mM stock solutions, diluted for the kinetic experiments) and $l = 10$ cm (gas phase, flow conditions), $\lambda = 200 - 320$ nm.

2.1. Henry's law coefficient of DMS

The Henry's law coefficient of DMS was determined from the equilibration of $DMS_{(gas)}$ with water and various aqueous solutions of NaCl (0.1, 1 and 4 M) at several temperatures and contact times with the liquid film in the WWFT, as shown in Fig. 1 (curve A) at 274.4 K for water (where 400 ml of a 1 mM stock solution of DMS in a bubbler served as reservoir of $DMS_{(gas)}$, passing the air through this solution directly into the WWFT). The flowtube was made of Duran glass and had an inner diameter of 0.6 cm with a movable inlet (by 140 cm) to vary the contact time. The movable gas inlet and outlet of the flowtube were made of PTFE tubing (outer diameter 0.6 cm, inner diameter 0.4 cm). A valve at the exit of the bubbler could be switched to alternatively monitor the level of $DMS_{(gas)}$ at the inlet or at the outlet of the WWFT connected by Teflon tubing to a 10 cm absorption cell in the spectrophotometer to observe the concentrations of DMS involved in the equilibrium $DMS_{(gas)} \rightleftharpoons DMS_{(aq)}$ from the spectra. Using an air

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flow of 70 ml/min and an aqueous flow of 3 ml/min the measurements were started after an equilibration time of at least 10 min. Then the absorption of DMS was monitored in the outflow of the WWFT at contact lengths up to 140 cm (varied every 6 min each), alternatively monitoring the corresponding absorption of DMS in the inflow each 6 min in the meantime (allowing 3 min for the equilibration each). Since the inflow level of DMS was observed to decrease exponentially with a lifetime of about 1 h, the values corresponding to the WWFT measurements were interpolated accordingly. Absorption spectra of the outflow and the inflow are shown in the inset of Fig. 1 (curves B). The interpolated consumption (circles in Fig. 1A) and a numerical model calculation describing the radial diffusive exchange of DMS between the gas-phase and the aqueous film using the software package FACSIMILE (AEA Technology, 1994; dashed curve) are included for comparison.

2.2. Heterogeneous kinetics

The WWFT technique, described in detail by Danckwerts, 1970, was used to determine the uptake coefficient, γ (the fraction of gas/liquid collisions that are effective in the uptake and/or chemical transformation; Hanson, 1997; Katrib et al., 2001), thus simulating chemical heterogeneous processes of the atmosphere experimentally in the laboratory, as discussed in detail in our previous work (Behnke et al., 1997, Frenzel et al., 1998). The heterogeneous aqueous-phase reaction of $O_{3(gas)}$ with $DMS_{(aq)}$ was studied by measuring the uptake of $O_{3(gas)}$ on various concentrations of $DMS_{(aq)}$ at different temperatures. The loss of O_3 in air (flow ~70 ml/min) was measured along the vertically aligned WWFT, the walls of which were conferred by a film of slowly flowing solutions of DMS (flow rate ~3.0 ml min^{-1}). The aqueous flow was controlled by a peristaltic pump and was adjusted to match the linear flow velocity of the gas. In the initial runs the pump caused a major loss of 80% of the DMS from the solution by its silicone rubber tubing until replacement by tygon tubing, that was found to be permeation resistant enough. As shown in Fig. 2, the data analysis can be approximated by the assumption that the uptake rate is first order with respect to the gas phase concentration of the reacting species, i.e.

$$C/C_0 = \exp[-k_{\mathrm{gas}}t], \quad (1)$$

where C_0 and C are the concentrations at the entrance and outlet of the flow tube respectively, t is the average gas contact time and k_{gas} is the first-order loss rate constant from the gas to the liquid phase. For small uptake coefficients, the rate constant k_{gas}, obtained from such a semilogarithmic plot is correlated to the uptake coefficient γ using the plug flow assumption (that is appropriate here because of the adjusted velocity of the film surface):

$$k_{\mathrm{gas}} = \gamma \cdot < c > /2r_{\mathrm{tube}}, \quad (2)$$

where $< c >$ is the average molecular speed of the gas and r_{tube} is the flowtube radius ($r_{\mathrm{tube}} = 3.0$ mm). The thickness of the aqueous film is less than 0.1 mm under our experimental conditions (Danckwerts, 1970). The molecular transport gas → liquid involves gas-phase diffusion and mass accommodation (α, the fraction of collisions with the surface that can lead to incorporation into the bulk liquid; Hanson, 1997) and the Henry's law coefficient (Herrmann et al., 2000). In this work it is considered that $\alpha \gg \gamma$, due the low uptake coefficient of O_3 ($\gamma = (1-15) \cdot 10^{-6}$) measured on the liquid film of DMS.

The uptake coefficient, γ, of O_3 for reactive penetration into the liquid depends on the solubility of the gas, i.e. Henry's law constant, H, the temperature, T, and the diffusion coefficient of O_3, D_{aq}, in aqueous phase. It is given by the equation

$$\gamma = \frac{\text{moelcules absorbed by the liquid layer}}{\text{molecules colliding with the liquid layer}} = \frac{4\,\mathrm{HRT}(k^1 \mathrm{D_{aq}})^{1/2}}{< c >}, \quad (3)$$

where $< c > = (8\,\mathrm{RT}/\pi\,\mathrm{M})^{1/2}$ and k^1 is the first-order loss rate constant of O_3 in the aqueous phase.

Figure 2 shows the uptake of O_3 (monitored by the Dasibi gas analyser) on various solutions of DMS at 274.4 K. The points represent the experimental measurements and the lines the results from a numerical model calculation (see below). For the Henry's law coefficient and the diffusion coefficient of $O_{3(aq)}$ the following data given by Kosak-Channing and Helz (1983) $H = 1.1 \cdot 10^{-2} \exp[(2300\,\mathrm{K}) \cdot (1/T - 1/T_0)]\ \mathrm{M\,atm^{-1}}$ (where $T_0 = 298\,\mathrm{K}$) and the dependence on ionic strength, μ, is given by the equation

$$\ln(H/\mathrm{M\,atm^{-1}}) = -2297T^{-1} + 2.659\mu + 688.0\mu T^{-1} + 12.19 \tag{4}$$

and $D_{aq} = 2.0 \cdot 10^{-2} \exp(-2200\,\mathrm{K/T})\ \mathrm{cm^2\,s^{-1}}$ given by Gershenzon et al. (2001) were used. The loss rate constant in the solution, k^I, depends on the concentration of the dissolved DMS, [DMS], according to the equation

$$k^I = k^{II} \cdot [\mathrm{DMS}], \tag{5}$$

where k^{II} is the rate constant for the aqueous-phase reaction

$$O_3 + \mathrm{DMS} \rightarrow \mathrm{DMSO} + O_2. \tag{R1}$$

For an improved interpretation of our data, we simulated the observed concentrations in the flowtube by a numerical model, described by Behnke et al., 1997. The one dimensional model (cylindrical coordinates), written in the FACSIMILE language (AEA Technology, 1994), includes radial diffusion in the gas and liquid phase and chemical reactions in the liquid phase. Axial diffusion is neglected, axial transport is described by progress in time. The lines in Fig. 2 from the model calculation are almost straight lines since there was a sufficient surplus of DMS over O_3 in these runs with the ozone analyser. The strength of the model calculation is that it can serve also for cases with lower ratios of $[\mathrm{DMS}]/[O_3]$ like those displayed in Fig. 3, where DMS is consumed almost completely. At high concentrations of DMS ($> 50\mu$M) it is possible to determine simultaneously the fast reaction that occurs in the surface of the liquid between O_3 and DMS and the liquid-gas equilibration of DMS (Henry's law coefficient) along the flow tube reactor by monitoring the spectra of both O_3 (Fig. 3 curves A) and DMS (Fig. 3, curves B) by the UV spectrophotometer.

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3. Results and discussion

3.1. Henry's law coefficient of DMS

The Henry's law coefficient of DMS on pure water was determined to be (in units of M atm^{-1}) H = 2.16±0.5 at 274.4 K, 0.72±0.2 at 291 K and 0.33±0.1 at 313.4 K; on 1.0 M NaCl we found H = 1.57±0.4 at 275.7 K and 0.80±0.05 at 313 K, and on 4.0 M NaCl H = 0.44±0.1 at 275.7 K and 0.16±0.04 at 291 K. These data are presented in Fig. 4 in comparison with literature data. The Henry's law coefficient of DMS was determined at different concentrations of NaCl, due to fact that NaCl is the major component of seasalt aerosol ([Cl$^-$] = 550 mM in seawater; Jaenicke, 1988), and also due to the importance of NaCl on a global scale (contributing about 60% of the natural sources of aerosol particles and more than 40%–60% to the natural aerosol mass, Pruppacher and Klett, 1997). The quantification of the Henry's law coefficient of DMS on high concentrations of NaCl (4.0 M NaCl) is of interest, considering that aerosols are usually solutions with molalities of NaCl ≥ 10 Mol/kg, therefore presenting very high ionic strengths (Tang, 1997). Our data on Henry's law coefficient can be described by Eq. (6):

$$\ln H = a \cdot T^{-1} + b \cdot \mu^2 + c \cdot \mu \cdot T^{-1} + d \tag{7}$$

with the parameters: $a = -4061 \pm 318$; $b = 0.052 \pm 0.030$; $c = 50.9 \pm 27.0$ and $d = 14.0 \pm 1.1$, where introducing a linear term $b \cdot \mu$ instead of $b \cdot \mu^2$ did not significantly improve the quality of the fit. Our data are much lower than the value of Lovelock et al. and about 30% higher than those of Hine and Weimar, Przyani et al., Dacey et al., and de Bruyn et al., confirming the dependence on molality observed by Dacey et al. (1984) and de Bruyn et al. (1995) and confirming the temperature dependence of the literature data. Due to the difficulties of handling the DMS solutions and determining the gaseous DMS levels (reference and after exposure to the water film) in an absorption cell connected via 2 m of Teflon tubing and the short wavelength of 202 nm employed for the detection of DMS (close to the short wavelength limit of the spectrophotometer, see Alebic-Juretic et al., 1991) this agreement with literature data must be considered as satisfactory.

3.2. Kinetic measurements

The rate constants determined by the WWFT in the present study are summarized in Table 2 in comparison with literature data. Figure 5 shows a compilation of all rate constants k^{II} obtained in this work for the reaction of O_3 with DMS in pure water in comparison with literature data and the respective temperature dependence. It should be noted that our model calculation neglects the axial diffusion in the gas phase that may become significant at the steep gradients at the very beginning of gas contact with the liquid film in the tube. Furthermore, our data in NaCl solution are lower than those in pure water, and this may partly be caused by an experimental problem with the smaller excess of DMS of those measurements. Another point is, that in our initial evaluation of the measurements on NaCl solutions our data at 1 M NaCl were about 10% lower than displayed in Fig. 5. Then we considered the slightly lower diffusion coefficients of the reactants in the saline solutions, known to be inversely proportional to the viscosity. At 20° C the viscosity of a 1 M NaCl solution is 9.5% higher than that of pure water (CRC Handbook, 1982), and the influence of salinity of seawater on viscosity is known to be slightly smaller at lower temperature (D'Ans-Lax, 1967). Considering this influence of a lower diffusion coefficient in 1M NaCl as compared to 0.1 M corrected the rate constants correspondingly upwards and brought the two series with NaCl into much better agreement. The measurements in pure water were obtained with a lower level of O_3 using an ozone analyser for detection and may thus represent more favourable conditions for the kinetic evaluation. Taking our data altogether we obtain an Arrhenius activation energy similar to that determined by Lee and Zhou (1994).

Our attempts to determine the rate constant directly in solution by the stopped flow method turned out to be unsuccessful (similar to a statement in the paper by Lee and Zhou), the reaction being too rapid to monitor the decay of O_3 in the presence of a surplus of DMS required for pseudo-first-order evaluation. With approximately equal concentrations of DMS and O_3 around 5 μM the absorption of ozone after a deadtime for mixing of about 1 ms disappeared with a lifetime of about 5 ms at 275 K. This corresponds to about $0.5 \cdot 10^8\ M^{-1}\ s^{-1}$ and confirms the rapid reaction in homogeneous aqueous solution.

Considering the slightly larger solubility of DMS obtained from the gas-phase observations of our study might indicate an underestimated loss of DMS from our system (by permeation, e.g.). Such an underestimated loss would decrease the observed rate constants slightly.

According to Gershenzon et al. (2001), the mechanism of the heterogeneous aqueous-phase reaction of O_3 with DMS can be interpreted mainly in terms of two complementary chemical factors: the chemical attack of the nucleophilic S on the electrophile O_3 and the participation of the solvent (acting as a polar adduct), facilitating the formation of DMSO. In contrast to DMS, DMSO $[(CH_3)_2S^+ - O^-]$ presents a polarised S-O bond, where DMSO acts (or is attacked) as an O-based nucleophile (or an S-based electrophile respectively), depending of course on the reaction partner.

4. Atmospheric implications

The chemistry and the transport/equilibration of DMS from gas to liquid phase represent an interesting subject for the understanding of the tropospheric heterogeneous reactions involving the aqueous phase, considering that the kinetics O_3 + DMS can be seen as a key reaction in comparison with other reactants, such as the radicals NO_3, OH, BrO and Cl, since it is an exceptionally fast aqueous-phase reaction and almost the only night-time sink of ozone in the chemistry of the remote marine boundary layer. In that respect DMS is expected to compete with bromide in the reaction of sea-spray with gaseous ozone as an antagonist of halogen activation in the aqueous phase. In the last 10 years, the high reactivity of halogens in the atmosphere has been studied with respect to their role in the well-known "ozone hole" where the interactions between gas and particulate phase and heterogeneous chemistry become important (Brasseur et al., 1999). On the other hand, DMS may act as a promoter of halogen activation in the gas-phase by supporting the recycling of BrO to the more ozone-reactive Br.

About the importance of the Henry's law coefficient for the troposphere, this coefficient is in direct connection with the study of the equilibria of species in terms of the cloud chemistry and aerosol formation at high salt concentrations. The laboratory simulation of the transport and reaction of a molecule such as DMS in aqueous phase is the first step for an understanding of the possible chemical and physical effects on this heterogeneous system and why enormous annual variations of the concentration of DMS are observed on the marine surface.

5. Conclusions

The correct understanding and simulation of the tropospheric heterogeneous aqueous-phase reactions and of the molecular gas/ liquid equilibrium (Henry's law quantification) are fundamentals for the use in global model calculations and for atmospheric chemistry. The heterogeneous aqueous phase reaction of O_3 with DMS is considered as an exception, because the gas phase reactions are normally fast compared to the same reaction in aqueous phase. As observed in this work and in agreement with previous work (Lee and Zhou, 1994; Gershenzon et al., 2001), the reaction of O_3 with DMS in aqueous phase is shown to be a factor of about one million faster than in gas phase, motivating this experimental study. We suppose that the heterogeneous reaction may interfere in the determination of gaseous DMSO in field measurements by denuders at high ozone levels and suggest that it constitutes a significant night-time sink of DMS, producing DMSO in the marine atmosphere where DMSO is further oxidised to H_2SO_4.

Another aspect of this work is that the experimental set-up and concept presented are completely different from others work (-bubbler-type gas-liquid reactor (Lee and Zhou, 1994) and horizontal bubble train apparatus (Gershenzon et al., 2001)), supplementing in this case the understanding of an important tropospheric reaction with this complementary and versatile technique (WWFT). A quantification of the Henry's law coefficient is also useful because of its impact (Crutzen and Lawrence, 2000) on

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precipitation scavenging during the transport of trace gases and implications on the meteorology and global changes.

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Table 1. Aqueous molar absorptivities and absorption cross section of O_3 and DMS

Molecule	λ/nm	$\varepsilon/M^{-1}\,cm^{-1}$ and $\sigma/cm^2\,molecule^{-1}$	working range
$O_{3(liquid)}$	258	$3000^{(a)}$	$4 - 15\,\mu M$
$O_{3(gas)}$	254	$1.14 \cdot 10^{-17(b)}$	$(0.2 - 50) \cdot 10^{14}$ molec $\cdot\, cm^{-3}$
$CH_3SCH_{3(liquid)}$	205	$1600^{(c)}$	$0.15 - 130\,\mu M$
$CH_3SCH_{3(gas)}$	202	$1.42 \cdot 10^{-17(d)}$	$(0.3 - 10) \cdot 10^{15}$ molec $\cdot\, cm^{-3}$

(a) von Gunten and Oliveras, 1998;
(b) Atkinson et al., 1997;
(c) Adewuyi and Carmichael, 1986;
(d) Hearn et al., 1990.

Table 2. Second-order rate constants (k^{II}) and estimated error limits Δk^{II} obtained in this work in comparison with literature data

	This work		Lee and Zhou, 1994		Gershenzon et al., 2001	
[NaCl]/M	$(k^{II} \pm \Delta k^{II})$/ 10^8 M^{-1} s^{-1}	T/K	k^{II}/ 10^8 M^{-1} s^{-1}	T/K	K^{II}/ 10^8 M^{-1} s^{-1}	T/K
0	4.1± 1.2	291	6.1	298	11	300
	2.15±0.65	283.4	3.3	288	8.6	293
	1.8±0.5	274.4	1.9	278	5.9	283
					5.1	274
0.1	3.2±1.0	288				
	1.7±0.5	282	–	–	–	–
	1.3±0.4	276				
1.0	3.2±1.0	288				
	1.3±0.4	282	–	–	–	–
	1.2±0.4	276				

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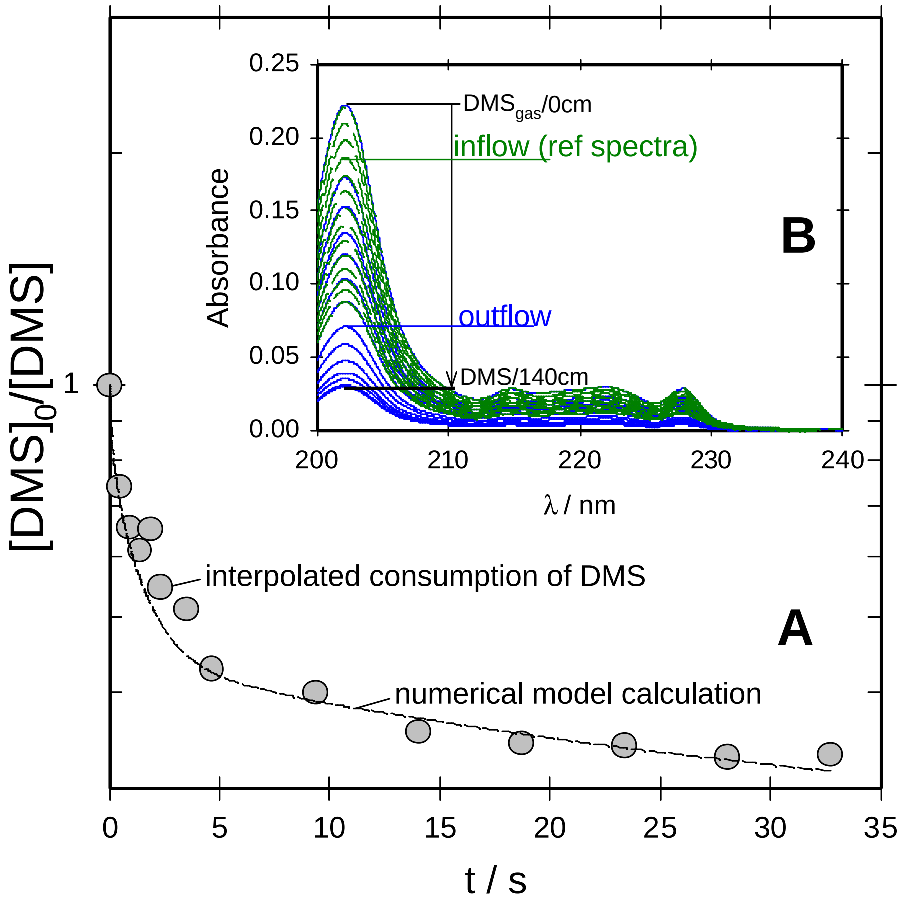

Fig. 1. Equilibration of DMS (gas) with water at 274.4 K at several contact times **(A)** that correspond to gas-liquid interaction lengths of 0, 2, 4, 6, 8, 10, 15, 20, 40, 60, 80, 100, 120 and 140 cm and the absorption spectra **(B)** of the inflow (green dashed curves) and the outflow (blue solid curves).

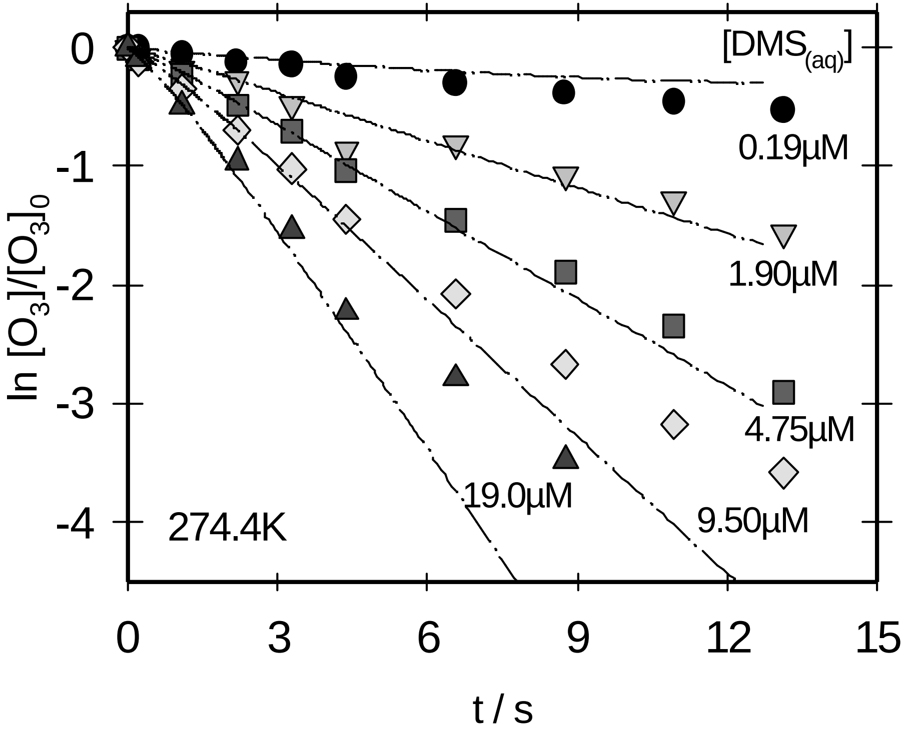

Fig. 2. Exponential decay of O_3 monitored by the ozone analyser (symbols) on various concentrations of DMS in comparison with a model calculation (curves).

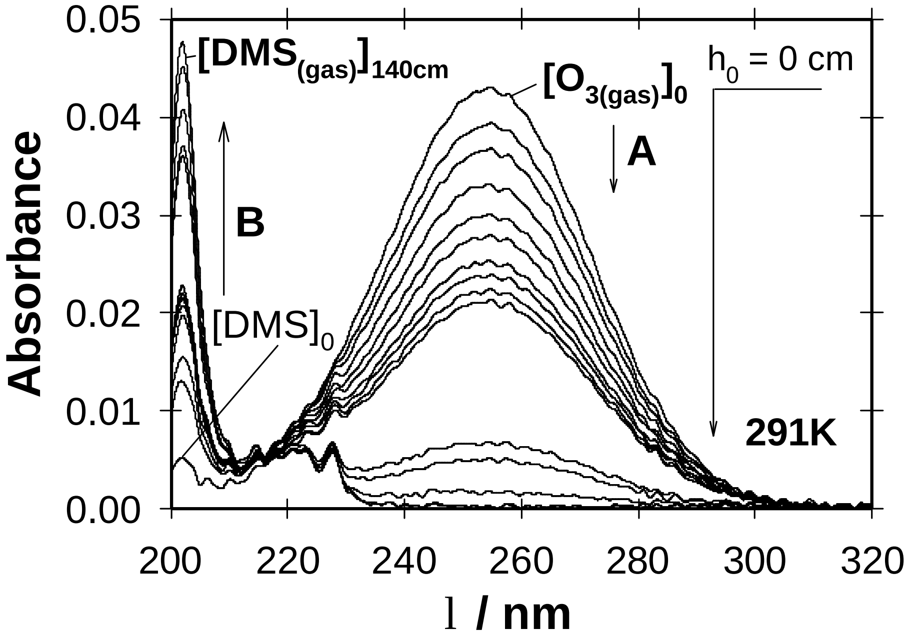

Fig. 3. Simultaneous spectral characterisation of the uptake of $O_{3(gas)}$ on $DMS_{(liq)}$ and the liquid-gas equilibration of DMS along the flowtube reactor. The spectra are displayed for contact lengths of 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 50, 100 and 140 cm.

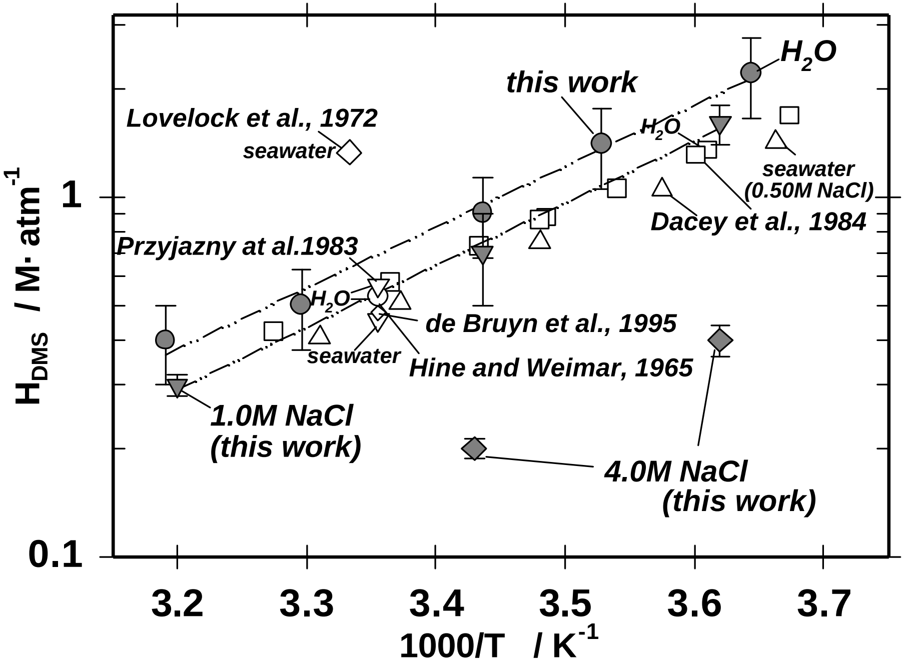

Fig. 4. Henry's law coefficients obtained in this work in comparison with literature data.

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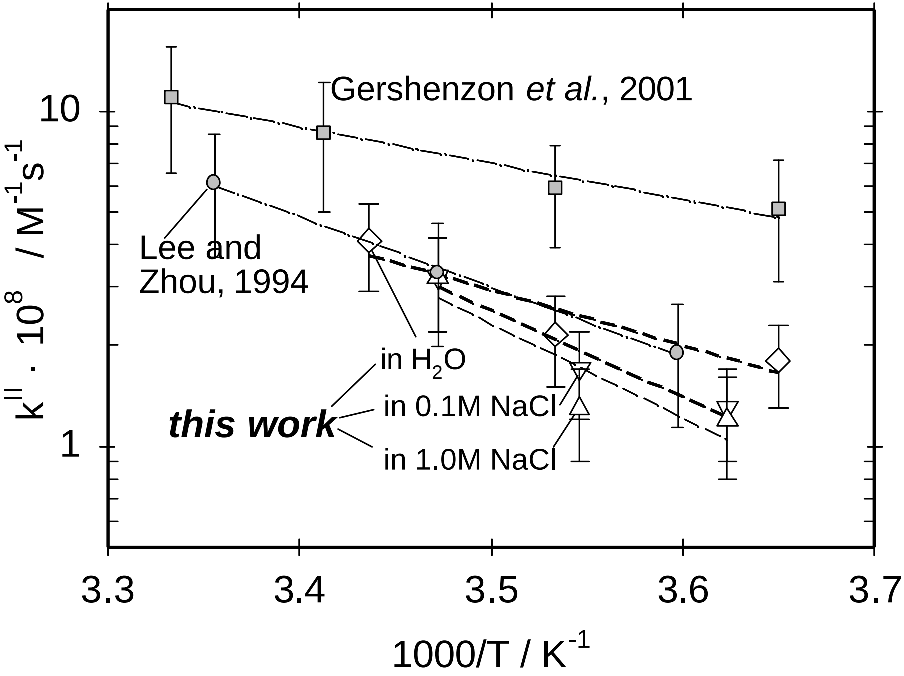

Fig. 5. Temperature dependence of the reaction of DMS with ozone in the aqueous phase observed in the present study (open symbols) in comparison with literature data (filled symbols) by Lee and Zhou (circles) and Gershenzon et al. (squares). Our data in pure water, 0.1 M NaCl and 1.0 M NaCl agree among each other within the error limits and confirm the earlier data by Lee and Zhou.